



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of:

Kamata et al.

Application No.: 10/539,283

Filed: December 17, 2003

Publication No.: 2006/0041053 A1

COLOR FILTER BLACK MATRIX RESIST
COMPOSITION AND CARBON BLACK
DISPERSION COMPOSITION USED FOR
THE COMPOSITION

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Sir:

Please enter this submission in the file of the above application. The following patents are being submitted for consideration by the Office:

1. U.S. Patent No. 5,378,274 to Yokoyama et al., issued January 3, 1995, from U.S. Patent Application No. 133,114, filed October 19, 1993;
2. U.S. Patent No. 5,176,971 to Shimamura et al., issued January 5, 1993, from U.S. Patent Application No. 742,457, filed August 5, 1991;
3. U.S. Patent No. 4,822,718 to Latham et al., issued April 18, 1989, from U.S. Patent Application No. 825,855, filed February 4, 1986;
4. U.S. Patent No. 5,527,649 to Sato et al., issued June 18, 1996, from U.S. Patent Application No. 249,754, filed May 26, 1994;

Application No.: 10/539,283

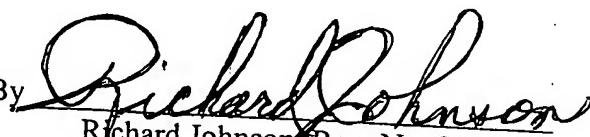
Publication No.: 2006/0041053 A1

5. U.S. Patent No. 5,998,090 to Sabnis et al., issued December 7, 1999, from U.S. Patent Application No. 982,233, filed December 1, 1997;
6. U.S. Patent No. 5,587,818 to Lee, issued December 24, 1996, from U.S. Patent Application No. 569,697, filed December 8, 1995;
7. U.S. Patent No. 5,780,201 to Sabnis et al., issued July 14, 1998, from U.S. Patent Application No. 721,841, filed September 27, 1996;
8. U.S. Patent No. 5,368,976 to Tajima et al., issued November 29, 1994, from U.S. Patent Application No. 36,253, filed March 24, 1993;
9. European Patent No. 0740183 to Nakamura et al., issued October 30, 1996, from European Application No. 96106302.1, filed April 22, 1996; and
10. Japanese Patent No. 08-034923 to Hatai, issued February 6, 1996, from Japanese Application No. 6-169507, filed July 21, 1994.

A check for the sum of \$180.00 is enclosed to cover the submission fee under 37 CFR 1.17(p).

The undersigned certifies that a copy of this submission has been sent by postage prepaid first class mail to Sughrue Mion, PLLC, 2100 Pennsylvania Avenue, N.W., Suite 800, Washington, DC 20037.

Respectfully submitted,

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US005378274A

United States Patent [19]

Yokoyama et al.

[11] Patent Number: 5,378,274

[45] Date of Patent: Jan. 3, 1995

[54] COLOR FILTER, METHOD FOR
MANUFACTURE THEREOF AND LIQUID
CRYSTAL PROJECTOR USING SAID
COLOR FILTER

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[21] Appl. No.: 133,114

[22] PCT Filed: Feb. 18, 1993

[86] PCT No.: PCT/JP93/00196

§ 371 Date: Oct. 19, 1993

§ 102(e) Date: Oct. 19, 1993

[87] PCT Pub. No.: WO93/17357

PCT Pub. Date: Sep. 2, 1993

[30] Foreign Application Priority Data

Feb. 19, 1992 [JP] Japan 4-031905

[51] Int. Cl.⁶ C09B 67/50

[52] U.S. Cl. 106/410; 106/411;
106/493; 106/494; 106/495; 106/497; 106/498;
252/582; 252/584; 252/585; 252/586; 359/885;
428/410

[58] Field of Search 359/885; 252/582, 584,
252/585, 586; 106/410, 411, 493, 494, 495, 497,
498; 428/410

[56] References Cited

U.S. PATENT DOCUMENTS

2,728,814 12/1955 Berger 359/885
3,104,176 9/1963 Hovey 359/885
4,786,148 11/1988 Sekimura et al. 359/885
4,934,791 6/1990 Shimizu et al. 252/582
5,185,074 2/1993 Yokoyama et al. 359/885

FOREIGN PATENT DOCUMENTS

0355585 2/1990 European Pat. Off. .
60-41086 3/1985 Japan .
60-129707 7/1985 Japan .
60-208704 10/1985 Japan .
62-89906 4/1987 Japan .
2-24603 1/1990 Japan .

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[57] ABSTRACT

Disclosed herein are a color filter wherein an organic pigment is comprised of primary particles having an average particle size of 20 to 200 nm and a particle size distribution within ± 35 nm and said organic pigment has a color difference of 5 or less when it is subjected to exposure at an illuminance of 100,000 lux or more for 100 hours or more under the condition of a surface temperature at 50° C.; a color filter wherein the film of coloring matter in green has a ratio (T_{485}/T_{610}) of the transmittance of 485 nm (T_{485}) to that of 610 nm (T_{610}) of 3.5 or less, the maximum transmittance of the film of coloring matter in green is 60% or more and said maximum transmittance is assigned a wavelength of 540 to 550 nm; and a color filter using a specific organic pigment as each of red, green and blue pigments.

5 Claims, 5 Drawing Sheets

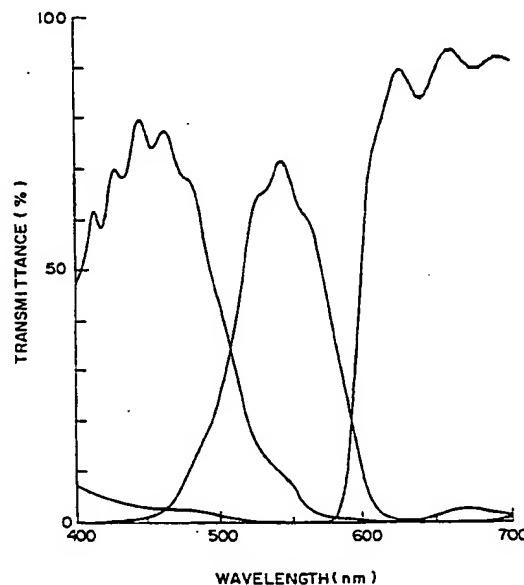


FIG. 1

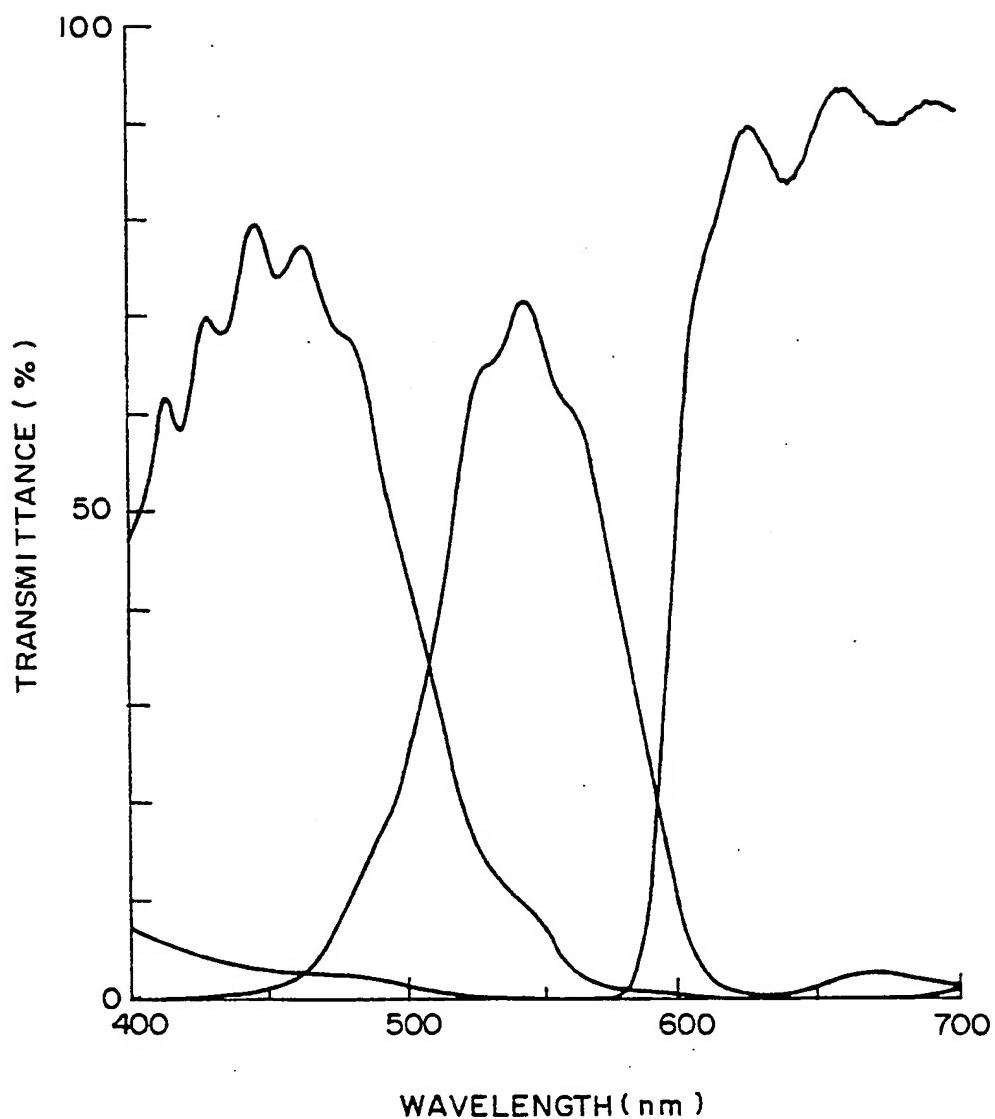


FIG. 2

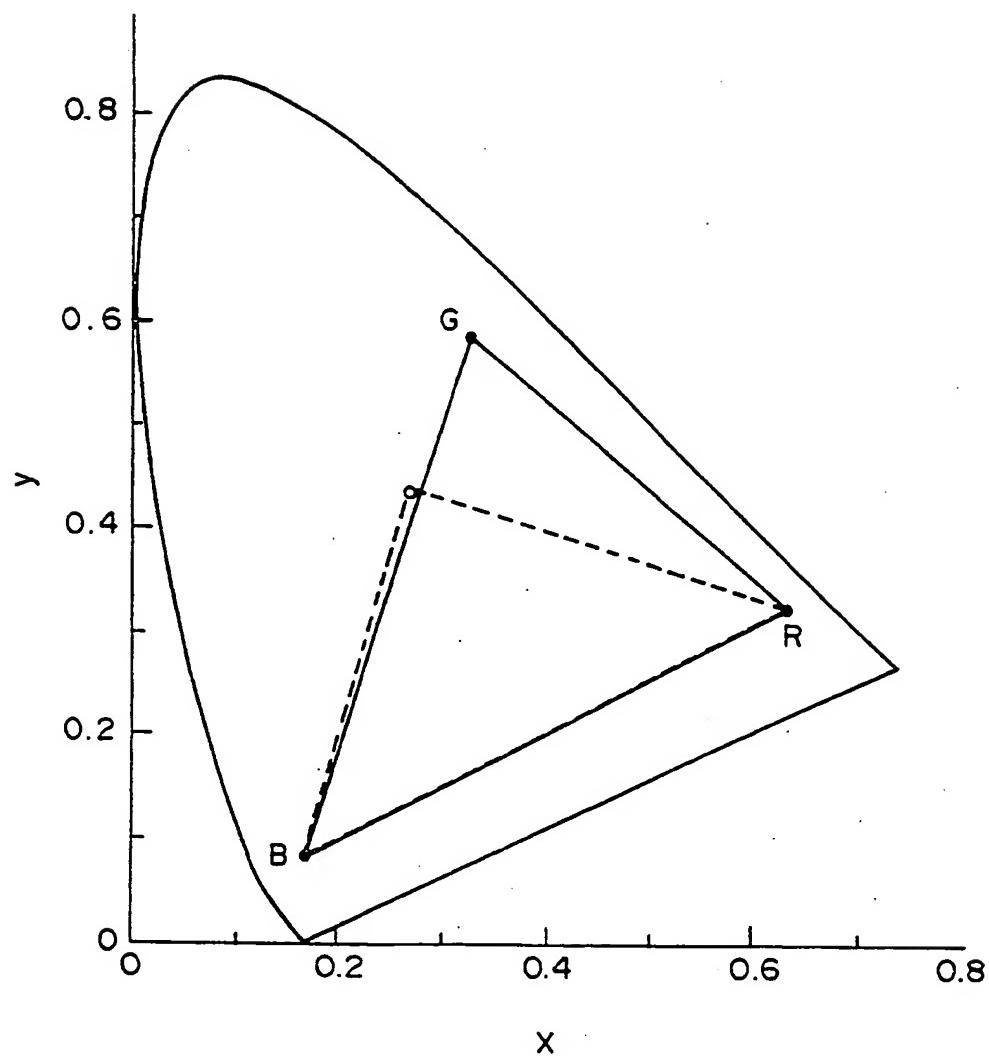


FIG. 3

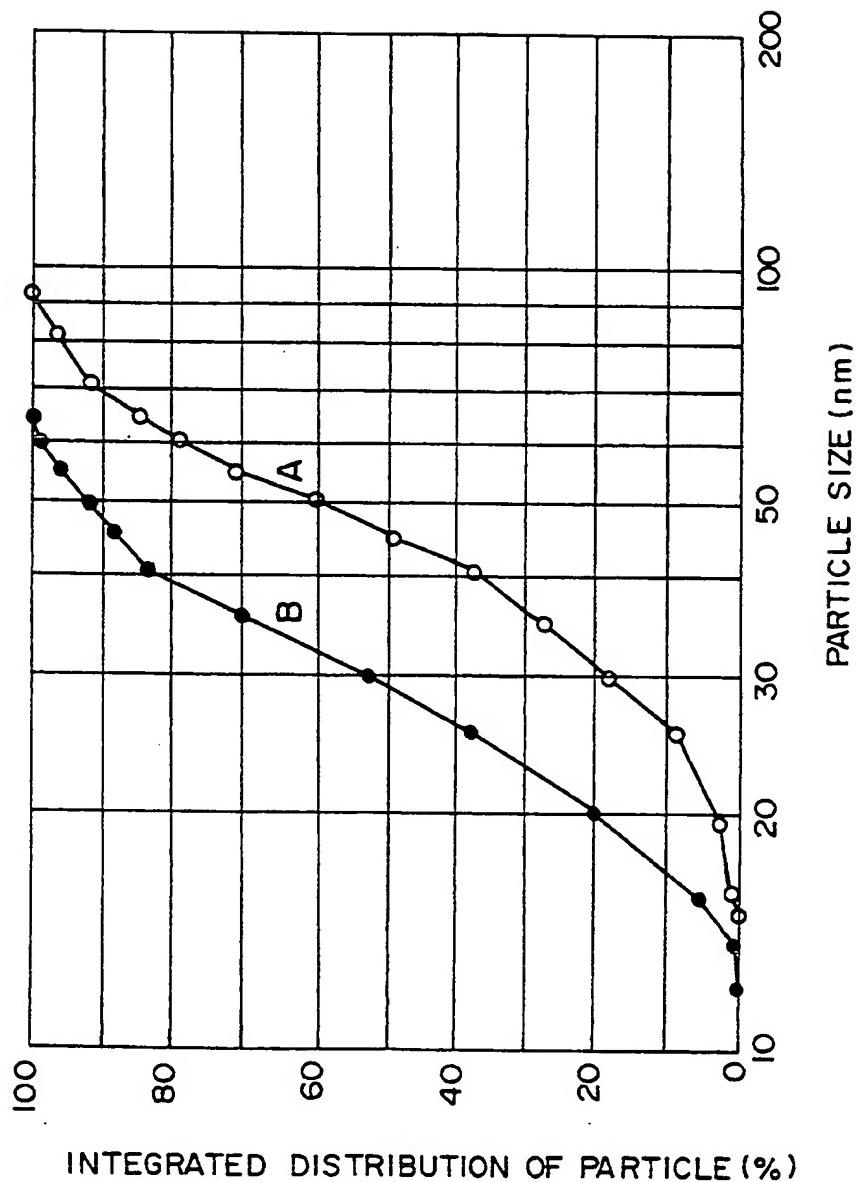


FIG. 4

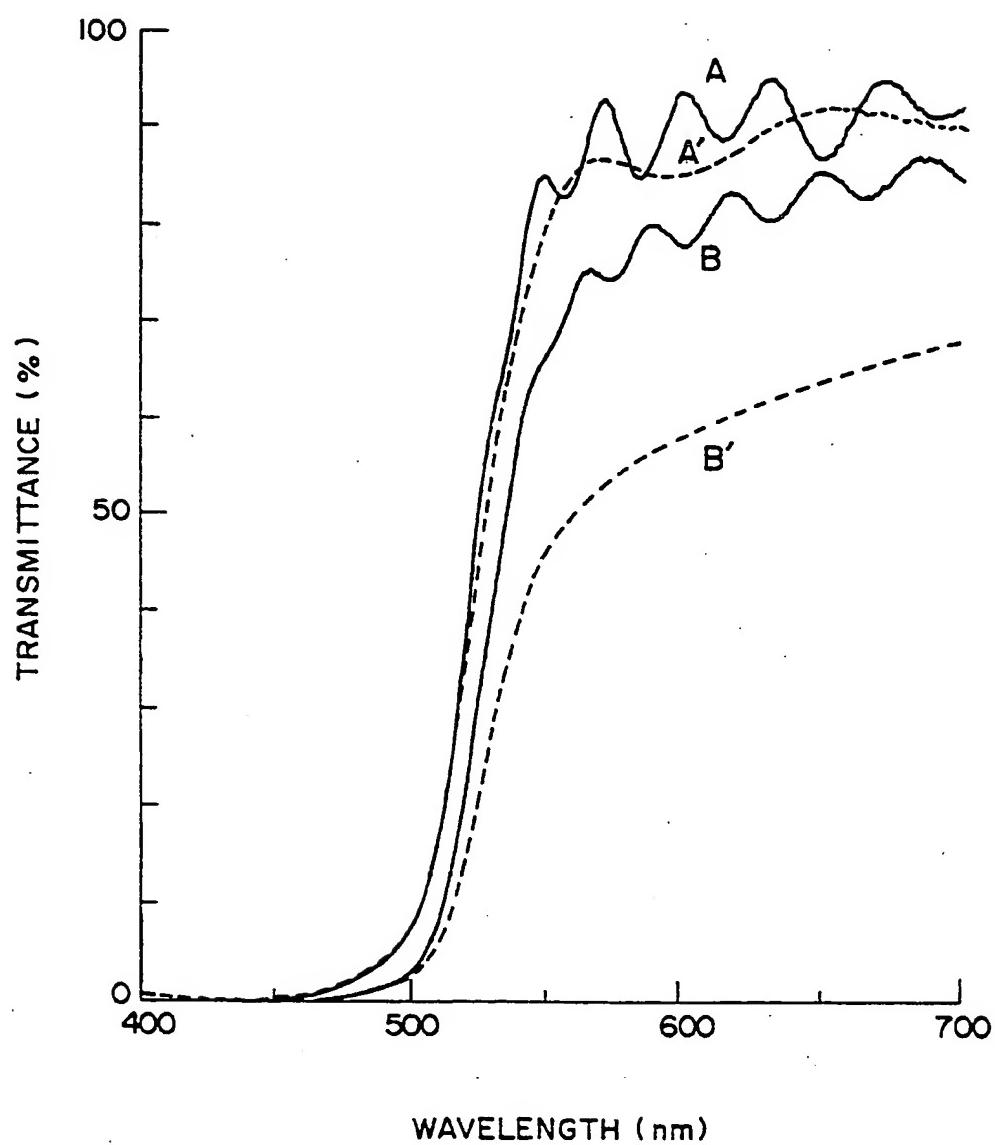
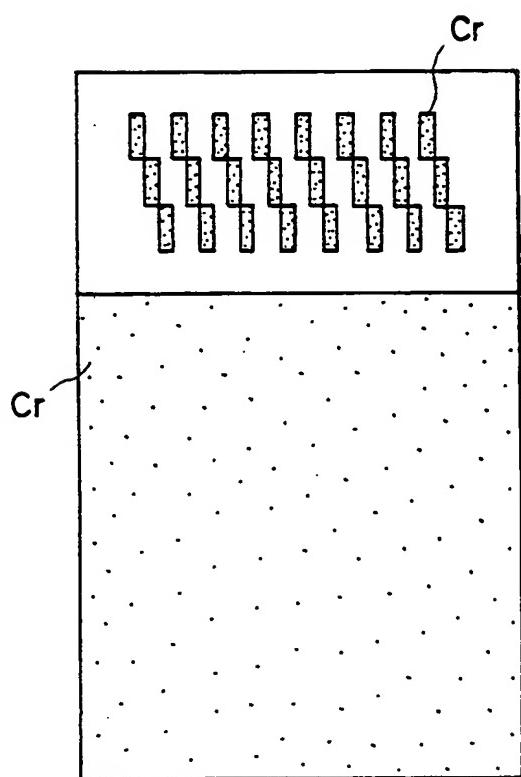


FIG. 5



COLOR FILTER, METHOD FOR MANUFACTURE THEREOF AND LIQUID CRYSTAL PROJECTOR USING SAID COLOR FILTER

TECHNICAL FIELD

The present invention relates to a novel color filter, a method for manufacture of said color filter and a liquid crystal projector using said color filter. More particularly, it relates to a color filter having a film of coloring matter in the three primary colors of red (R), green (G) and blue (B), excellent light resistance and heat resistance and capable of withstanding the use of highly bright light sources, a method for efficiently manufacturing said color filter according to the micellar disruption method and a liquid crystal projector using said color filter which has a long life and is economically advantageous.

BACKGROUND ART

In recent years, color displays of image in liquid crystal television sets, personal computers of lap top type and so on have been advanced by the development of multicolor display devices comprising a linear electrode-simple matrix, time-sharing drive or an active matrix drive wherein every picture element is incorporated with a thin film transistor (TFT).

Some of these developments have already been merchandised as a small size color liquid crystal television set.

These multicolor display devices use color filters having films of coloring matter in the three primary colors of RGB. Conventionally, the color filters have been manufactured according to various methods. For example, the dyeing method (Japanese Patent Application Laid-Open No. 55301/1985), the printing method (Japanese Patent Application Laid-Open No. 46325/1983 and Japanese Patent Application Laid-Open No. 29225/1984), the pigment dispersion method (Japanese Patent Application Laid-Open No. 237403/1985), the electrodeposition method (Japanese Patent Application Laid-Open No. 270730/1986), the vapor deposition method (Japanese Patent Application Laid-Open No. 166607/1980), the micellar disruption method (Japanese Patent Application Laid-Open No. 243298/1988 and Japanese Patent Application Laid-Open No. 50538/1988 through PCT) and so on have been known. The color filters thus manufactured have widely been used as the liquid crystal display material in liquid crystal television sets (Japanese Patent Application Laid-Open No. 7886/1986), personal computers of lap top type (Japanese Patent Application Laid-Open No. 105613/1985) and so on.

Meanwhile, liquid crystal projectors such as liquid crystal television projector, overhead projector and video projector have attracted attention as a large size display apparatus to replace color CRTs, and their development has been sped up in recent years. There have been known two types of liquid crystal projector. One of them is a projector of single plate type (Japanese Patent Application Laid-Open No. 41086/1985) and another a projector of three plate type (Japanese Patent Application Laid-Open No. 306792/1988). However, the devices of single plate type have a short life because of conventional color filters all of which are poor in light resistance and it is necessary that these devices be improved so as to prolong the service life. On the other hand, the liquid crystal projectors of three plate type

have the drawbacks that their manufacturing cost is at a high side because they have to have an equivalent to 3 sets each of optical system and dichroic mirror and that the optical system is a complicated one.

- 5 Thus, it is necessary that a color filter excellent in light resistance be developed. Liquid crystal projectors of single plate type capable of using strong light sources will be made available by the use of color filters having excellent light resistance if such color filters come true.
 10 In addition, liquid crystal panels for overhead projector and for car will be permitted to use strong backlighting with the improved color filters, to have elevated reliability and a significantly longer life.

In color filters, the light is shielded respectively in part of the wavelengths ascribed to every color to generate the heat. Accordingly, highly bright light sources applied to color filters gives rise to the elevation of temperatures on the surface of the color filters. If still brighter light sources are used to obtain clearer pictures, the temperatures on the surface of the color filters are brought up even higher, and thus light resistance under further elevated temperature conditions is required.

25 Conventionally, it has been known that mixed systems of pigments denoted by the following Color Index Pigment Number (C.I.P.) are used as the organic pigment of color filters having high light resistance as disclosed in Japanese Patent Application Laid-Open No. 89906/1987:

- 30 :9, 97, 122, 123, 149, 168, 177, 180, 192, 215 216, 217,
 220, 223, 224, 226, 227, 228, 240
 Yellow (Y) :20, 24, 86, 93, 109, 110, 117, 125, 137, 138,
 147, 148, 153, 154, 166, 168
 Green (G) :7, 36
 Blue (B) :15, 15:6, 22, 60, 64
 Violet (V) :19, 23, 30, 37, 40, 50

However, liquid crystal projectors developed recently have a 3~5 inch panel to be magnified to the size of 40~200 inches, and it is necessary to project on the panels by the use of very strong light sources. It is known that projections are converged with microlenses attached to picture element. In these liquid crystal projectors, the projections are converged in this way, requiring the passage of the light of 100,000 lux or more through color filters, and it is impossible that all of above-mentioned organic pigments can withstand the use of light sources as strong as above. Thus, a color filter resistant to light sources of 100,000 lux or more, preferably 500,000 lux or more and more preferably 1,000,000 or more is desired. The necessity is particularly urgent in the red and green colors which are susceptible to the quick deterioration.

DISCLOSURE OF THE INVENTION

Under these circumstance, the present inventors have made intensive studies with a view to developing a color filter excellent in light resistance and capable of withstanding the use of said highly bright light sources which are preferably used in liquid crystal projectors, large size internal liquid crystal panels for car and so on, a method for efficiently manufacturing said color filter and a liquid crystal projector using said color filter to have a long life. As the result, they have had the following findings:

At first, pigments were chosen on the basis of light resistance against the use of said highly bright light sources. Specifically, it was found that there is sufficient

light resistance in C.I. Pigment Red 168 (anthanthrone-based pigment), C.I. Pigment Red 177 (dianthraquinine-based pigment), C.I. Pigment Yellow 110 (isoindolinone-based pigment), C.I. Pigment Green 7 (chlorocopperphthalocyanine-based pigment), C.I. Pigment Green 36 (chlorobromocopperphthalocyanine-based pigment), C.I. Pigment Blue 15:3, 15:4 (monochlorocopperphthalocyanine-based pigment), C.I. Pigment Blue 15:6 (monochlorocopperphthalocyanine-based pigment) and C.I. Pigment Violet 23 (dioxane-based pigment). Furthermore, the red and green were found to be susceptible to the quicker deterioration than the blue by far. The cause for the deterioration was investigated to determine that the yellow pigments used to adjust the color tone of the red or green are liable to deteriorate significantly. Thus, it was found that color filters can be made light resistant as a whole by using as the red (R) a single C.I. Pigment Red 168 or a single C.I. Pigment Red 177 or a mixed system pigment combining C.I. Pigment Red 168 with C.I. Pigment Yellow 110 or a mixed system pigment combining C.I. Pigment Red 177 with C.I. Pigment Yellow 110; as the green (G) a mixed system pigment combining C.I. Pigment Green 7 or C.I. Pigment Green 36 with C.I. Pigment Yellow 110; and as the blue (B) a mixed system pigment combining C.I. Pigment Blue 15:3, 15:4 or 15:6 with C.I. Pigment Violet 23.

For conventional color filters, their pigments were chosen giving priority to spectral properties. These color filters were poorly resistant to the light when they were subjected to exposure by the use of intensely bright light sources. Furthermore, even some of the light resistant pigments including those disclosed in Japanese Patent Application Laid-Open No. 89906/1987 were found not to have sufficient spectral properties when they were used along with the intensely bright light sources as set forth above. As evident from these findings, it is essential that the pigments chosen as above be used as a light resistant pigment when intensely bright light sources are participated.

On the other hand, an attempt was made to obtain improved light resistance from a measure of light resistance inherent in certain pigments. In the pigments comprised of primary particles having a wide particle size distribution from coarse to fine, the light helped particles grow fast, and when the light was irradiated to these particles, their colors were liable to change significantly. It was found on the basis of this knowledge that where there is high transparency of pigments whose primary particles have an average size in a range of 20~200 nm, preferably 20~150 nm and more preferably 20~100 nm, the said pigments can obtain markedly improved light resistance by controlling the particle size distribution to be within ± 35 nm to obtain the uniform particles and thus preventing the growth of 55 particles due to the light.

Furthermore, the films of coloring matter in the green are different from those of the red or blue in that light shielding is not sufficient if merely the light having a wavelength longer or shorter than a certain wavelength is restrained from the transmission. For the green color films, well-balanced light shielding should be achieved by blocking both the wavelengths ascribed to the red and the wavelengths ascribed to the blue simultaneously. Accordingly, it is necessary to prevent the lights having a wavelength of 485 nm or shorter and a wavelength of 610 nm or longer from transmission and therefore to shield the transmitted light at 485 nm or

shorter by the yellow and that at 610 nm or longer by the green. More specifically, a ratio (T_{485}/T_{610}) of the transmittance at 485 nm (T_{485}) to that at 610 nm (T_{610}) need to be 3.5 or less, preferably 3.0 or less and more preferably 0.5~3.0.

Furthermore, the lights having wavelengths ascribed to RGB at the light source should be used effectively to the full extent to bring the characteristics of the color filters to work satisfactorily. For this, it is necessary to maximize the integrated quantity of transmitted light at the wavelength ascribed to each color of RGB. More specifically, each color film should have the maximum transmittance of 60% or more, preferably 65% or more and more preferably 70% or more. Particularly, in order to maximize the integrated quantity of transmitted light in green, the maximum transmittance of the green is assigned the wavelengths in a range of 540~550 nm.

Briefly, the films of coloring matter in green having very good spectral properties can be obtained by choosing the appropriate pigments, adjusting their mixing ratio and classifying their particles. The green color films thus produced have a ratio (T_{485}/T_{610}) of the transmittance at 485 nm (T_{485}) to that at 610 nm (T_{610}) of 3.5 or less, preferably 3.0 or less and more preferably 0.5~3.0, while the maximum transmittance of the film of coloring matter in green is 60% or more, preferably 65% or more and more preferably 70% or more and said maximum transmittance is assigned the wavelengths in a range of 540 to 550 nm.

Of the yellow organic pigments as defined above, the C.I. Pigment Yellow 110 (isoindolinone-based pigment) was found to be preferably used as the yellow pigment to adjust the color tone of either or both of the red and green. It was also found that above-mentioned spectral properties can be obtained by using a mixture of C.I. Pigment Green 36 (chlorobromophthalocyanine-based pigment) and C.I. Pigment Yellow 110 (isoindolinone-based pigment) as the green.

Meanwhile, the micellar disruption method is free of binder resins, helpful to obtain excellent heat resistance and light resistance and improves depolarizing properties which are an important problem to compounds of the pigment series. Therefore, the micellar disruption method is particularly preferred in the manufacture of color filters, although any one of the pigment dispersion method, the printing method and the micellar disruption method is suitable.

However, it should be pointed out that the conventionally known method for the preparation of organic pigment dispersions as disclosed in Japanese Patent Application Laid-Open No. 243298/1988 and Japanese Patent Application Laid-Open No. 30794/1990 is not good enough to manufacture the color filters excellent in light resistance from organic pigments according to the micellar disruption method. To provide organic pigments comprising primary particles having an average particle size of 200 nm or smaller, a surfactant comprising a ferrocene derivative, an organic pigment and a supporting salt are mixed in an aqueous medium; the resultant mixture is dispersed for 0.5 hour or more per liter, preferably 0.5~2 hours per liter in the presence of ultrasonic waves by the use of a ultrasonic dispersing device of 50 W or more, preferably 300 W or more and more preferably 600 W or more; and the dispersion formed as above is centrifuged with a centrifugal force of $4000 \times g$ (g denotes the acceleration of gravity) or more, to be followed by filtration if necessary. In this way, the dispersion is made to contain the pigments

whose primary particles are classified to have the average particle size in the range of 20~200 nm and a particle size distribution within ± 35 nm. The color filters having excellent light resistance can be obtained only when their films are formed of this dispersion of organic pigment according to the micellar disruption method.

The present invention has been completed on the basis of such findings. Accordingly, the present invention provides (1) a color filter having a film of coloring matter in the three primary colors of red, green and blue, wherein the organic pigments forming the film of coloring matter in each of red, green and blue are comprised of primary particles having an average particle size of 20~200 nm and a particle size distribution within ± 35 nm and furthermore said organic pigments have a color difference of 5 or less after said pigments as contained in color filters are subject to exposure for 100 hours or more at an illuminance of 100,000 lux or more by the use of a highly bright light source for projection under the condition of a surface temperature at 50° C. or higher, (2) a color filter having a film of coloring matter in the three primary colors of red, green and blue, wherein the film of coloring matter in green has a ratio (T_{485}/T_{610}) of the transmittance at 485 nm (T_{485}) to that at 610 nm (T_{610}) of 3.5 or less, the maximum transmittance of the film of coloring matter in green is 60% or more and said maximum transmittance is assigned the wavelengths in a range of 540 to 550 nm, and (3) a color filter having a film of coloring matter in the three primary colors of red, green and blue, wherein the red (R) coloring matter is a single C.I. Pigment Red 168 or a single C.I. Pigment Red 177 or a mixed system pigment combining C.I. Pigment Red 168 with C.I. Pigment Yellow 110 or a mixed system pigment combining C.I. Pigment Red 177 with C.I. Pigment Yellow 110; the green (G) coloring matter is a mixed system pigment combining at least one compound selected from the group consisting of C.I. Pigment Green 7 and C.I. Pigment Green 36 with C.I. Pigment Yellow 110; and the blue (B) coloring matter is a mixed system pigment combining at least one compound selected from the group consisting of C.I. Pigment Blue 15:3, 15:4 and 15:6 with C.I. Pigment Violet 23. The present invention also provides a color filter as defined in (1) and (2) above, wherein preferably the C.I. Pigment Yellow 110 is used as a yellow pigment to adjust the color tone of either or both of red and green of organic pigments and a color filter as defined in (2) above, wherein preferably a mixture of C.I. Pigment Yellow 110 and C.I. Pigment Green 36 is used as a pigment to adjust the color tone of at least green of organic pigments.

The present invention further provides a method for manufacturing the color filter as defined in (1), (2) or (3) above, which comprises dispersing each of red, green and blue pigments in an aqueous medium by the use of a surfactant comprising a ferrocene derivative to prepare a dispersion, dipping into any one of the dispersions formed as above a substrate for manufacture of color filter which has a transparent electroconductive thin film on an electrically insulating substrate, electrifying said substrate to form a film of coloring matter on an electrode of said substrate; repeating the foregoing procedure successively for each of the remaining two dispersions; and thereby forming on said substrate the films of coloring matter in the three primary colors of red, green and blue. The present invention further provides the manufacturing method as defined above, which preferably comprises mixing a surfactant com-

prising a ferrocene derivative, an organic pigment and a supporting salt in an aqueous medium, dispersing said mixture for 0.5 hour or more per liter in the presence of ultrasonic waves by the use of a ultrasonic dispersing devices with an output of 300 W or more, centrifuging the dispersion formed above with a centrifugal force of $4000 \times g$ or more, and thus forming a dispersion containing organic pigment whose primary particles are classified to have an average particle size in the range of 20~200 nm and a particle size distribution within ± 35 nm.

The present invention still further provides a liquid crystal projector using the color filter as defined in (1), (2) or (3) above.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graph showing spectral properties of the color filter obtained in Example 1.

FIG. 2 is a graph showing the chromaticity coordinates before and after the light was irradiated to the color filter obtained in Comparative Example 2.

FIG. 3 is a graph showing the particle size distribution of the primary particles of organic pigments in the pigment dispersions obtained in Preparation Examples 6 and 7.

FIG. 4 is a graph showing the spectral transmittance before and after the light was irradiated to the film of coloring matter obtained in Example 11 and Comparative Example 9.

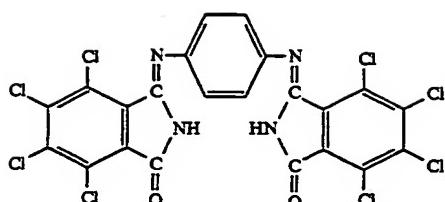
FIG. 5 is a schematic diagram illustrating a mask designed to prepare a taken-out electrode mounting.

BEST MODE FOR CARRYING OUT THE INVENTION

The first color filters of the present invention have the films of coloring matter in the three primary colors of RGB. The film of coloring matter in each color of RGB comprises organic pigments whose primary particles have an average particle size in the range of 20~200 nm, preferably 20~150 nm and more preferably 20~100 nm and a particle size distribution within ± 35 nm. These organic pigments have a color difference of 5 or less after said organic pigments as contained in color filter are subjected to exposure for 100 hours or more at an illuminance of 100,000 lux or more by the use of a highly bright light source for projection under the condition of a surface temperature at 50° C. or higher. Thus, these organic pigments are capable of withstanding the use of highly bright light sources.

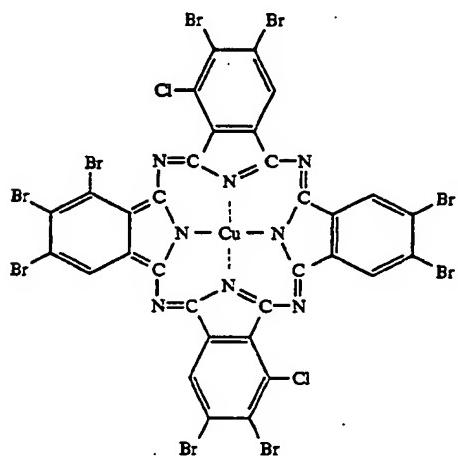
The second color filters of the present invention have the films of coloring matter in the three primary colors of RGB, particularly comprising the color film in green having very good spectral properties. Said film of coloring matter in green has the ratio (T_{485}/T_{610}) of the transmittance at 485 nm (T_{485}) to that at 610 nm (T_{610}) of 3.5 or less, preferably 3.0 or less and more preferably 0.5~3.0, the maximum transmittance of the film of coloring matter in green is 60% or more, preferably 65% or more and more preferably 70% or more and said maximum transmittance is assigned the wavelengths in the range of 540~550 nm.

In these first and second color filters, the C.I. Pigment Yellow 110 (an isoindolinone-based pigment) as represented by the following formula:

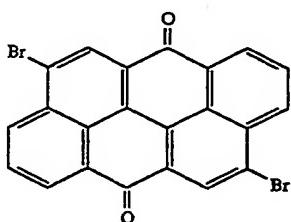


is used as a yellow pigment to adjust the color tone of either or both of red and green, enabling the color filters to exhibit excellent effects.

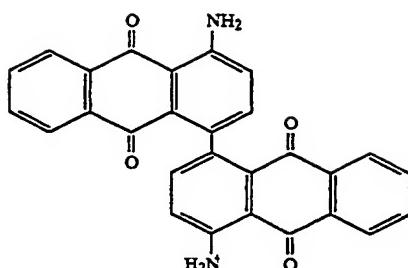
In said second color filters, a mixture of said C.I. Pigment Yellow 110 and C.I. Pigment Green 36 (a chlorobromocopperphthalocyanine-based pigment) as represented by the following formula:



is used as a pigment to adjust the color tone of at least green, and thus said spectral properties can be obtained with ease. Furthermore, the third color filters of the present invention have the films of coloring matter in 45 the three primary colors of RGB, and as the coloring matters in red, green and blue, each of following specific pigments should be used. As the red coloring matter, a single C.I. Pigment Red 168 (an anthanthrone-based pigment) as represented by the following formula:



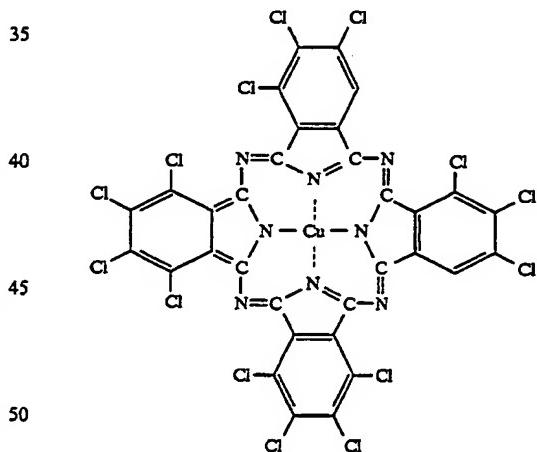
or a single C.I. Pigment Red 177 (a dianthraquinone-based pigment) as represented by the following formula:



15 or a mixed system pigment combining said C.I. Pigment Red 168 with C.I. Pigment Yellow 110 or a mixed system pigment combining said C.I. Pigment Red 177 with C.I. Pigment Yellow 110 should be used.

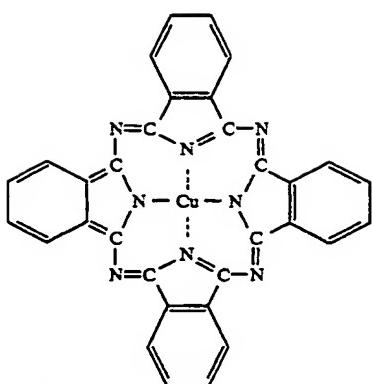
It is preferable that these mixed systems of red pigment contain 50% or more by weight of C.I. Pigment Red 168 or C.I. Pigment Red 177.

20 25 As the green coloring matter, for example a mixed system pigment combining at least one compound selected from the group consisting of C.I. Pigment Green 30 7 (a chlorocopperphthalocyanine-based pigment) as represented by the following formula:

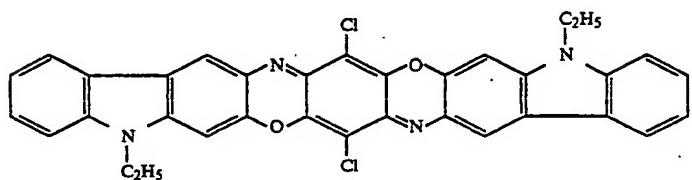


35 40 and said C.I. Pigment Green 36 with said C.I. Pigment 55 Yellow 110 should be used. It is preferable that this mixed system of green pigment contain 40% or more by weight of the C.I. Pigment Green 7 or C.I. Pigment Green 36.

60 65 As the blue coloring matter, for example a mixed system pigment combining at least one compound selected from the group consisting of C.I. Pigment Blue 15:3, 15:4 and 15:6 (each being a chlorocopperphthalocyanine-based pigment) as represented by the following formula:



with C.I. Pigment Violet 23 (a dioxane-based pigment) as represented by the following formula:



should be used. It is preferable that this mixed system of blue pigments contain 70% or more by weight of at least one compound selected from the group consisting of C.I. Pigment Blue 15:3, 15:4 and 15:6.

In so far as their films of coloring matter in the three primary colors of RGB are prepared from the red, green and blue pigments as defined above, the color filters having these color films in the three primary colors of RGB are excellent in light resistance, capable of withstanding the use of highly bright light sources and further superior in spectral properties.

The method for manufacturing the color filter of the present invention is not particularly limited. Any method can optionally be chosen from among those conventionally known, for example, the dyeing method, the printing method, the pigment dispersion method, the electrodeposition method, the vapor deposition method, the micellar disruption method and the like. Of them, however, the micellar disruption method is preferred. The color filters whose color films in the three primary colors of RGB are formed by the use of micellar disruption method have less depolarizing properties and further are excellent in heat resistance and light resistance because these color filters are free of binder resins.

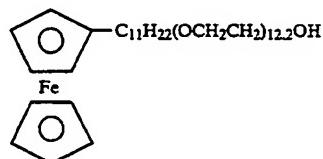
The manufacture of the color filters according to the micellar disruption method is not particularly limited, but any conventionally known variations in the method may find their places. However, the color filters can be efficiently manufactured according to the following method of the present invention.

The method for manufacturing the color filter of the present invention will be described below. The method of the present invention comprises manufacturing the color filters by forming the films of coloring matter in the three primary colors of RGB on a transparent electroconductive thin film laid on a substrate for manufacture of color filter which is made of an electrically

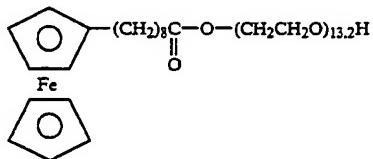
insulating substrate with said transparent electroconductive thin film thereon.

According to the method of the present invention, a red pigment, a green pigment and a blue pigment as desired are respectively dispersed in an aqueous medium by the use of a surfactant comprising a ferrocene derivative (a micelle forming agent) to prepare the dispersions. AS an aqueous medium used in this process, various media such as water, a mixture of water and alcohol, a mixture of water and acetone and so on can be mentioned.

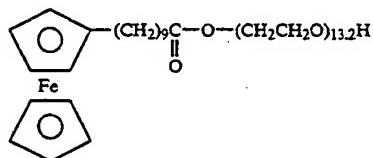
As a ferrocene derivative used as a surfactant in preparing said dispersion, various ferrocene derivatives can be mentioned, including those of ammonium type, ether type, ester type and so on. Their typical examples include a FPEG represented by the following formula:



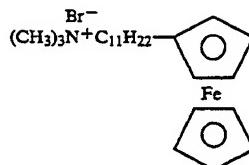
a FEST8 represented by the following formula:



a FEST9 represented by the following formula:



and a FTMA represented by the following formula:



Mentioned below is the oxidation-reduction potential of these micelle forming agents comprising the ferrocene derivatives mentioned as above:

Oxidation-reduction potential:

FPEG: 0.25V
FEST8: 0.19V
FEST9: 0.22V
FTMA: 0.14V

Besides those mentioned above, the method of the present invention can use the ferrocene derivatives produced according to the processes described in the specification of International Patent Application W089/01939, and in Japanese Patent Application Laid-Open No. 45370/1989, Japanese Patent Application Laid-Open No. 226894/1989, Japanese Patent Application Laid-Open No. 83387/1990, Japanese Patent Application Laid-Open No. 250892/1990 and the like.

As the surfactant used in the method of the present invention, said ferrocene derivatives may be used alone or as combination of at least two of them and, if necessary a combination of said Ferrocene derivatives with other surfactants may as well be used. As the other surfactant, for example nonionic surfactants such as polyoxyethylene alkyl ether, polyoxyethylene fatty acid ester, polyoxyethylene alkyl phenyl ether, polyoxyethylene polyoxypropylene alkyl ether and so on can be preferably mentioned. Further, cationic and anionic surfactants such as alkyl sulfate, polyoxyethylene alkyl ether sulfate, alkyltrimethyl ammonium salt, fatty acid diethylaminoethylamide and so on can be used.

It is advantageous that the dispersions of pigment used in the method of the present invention be prepared in the following way. At first, a surfactant comprising a ferrocene derivative as mentioned above, an other surfactant as desired, various organic pigments and a supporting salt are placed and mixed in an aqueous medium. The resultant mixture is dispersed for 0.5 hour or more per liter, preferably 0.5~2 hours per liter in the presence of ultrasonic waves by the use of a ultrasonic dispersing device with an output of 50 W or more, preferably 300 W or more and more preferably 600 W or more. The dispersion formed as above is centrifuged with a centrifugal force of 4000×g or more and filtered if necessary to obtain a dispersion of organic pigments whose primary particles are classified to have an average particle size of 20~200 nm and a particle size distribution within ±35 nm.

The concentration of the surfactants used in the process is not particularly limited. Ordinarily, the concentration of said ferrocene derivative and that of the other surfactant used as desired are chosen from a range that exceeds the critical micelle concentration, preferably the range of the equilibrium of total critical micelle concentrations to 3 mmol/liter.

On the other hand, the concentration of each pigment is ordinarily chosen from the range of 1~500g/liter.

Said supporting salt is added to control the electrical conductivity. The amount of the supporting salt to be added may be the range that does not prevent the deposition of the pigments dispersed therein, but usually a concentration in the range of 0.01~2.00 mmol/liter is ordinarily chosen. Electrolysis may be carried out without using the supporting salt, and in this case, a high purity thin film free from supporting salt can be prepared.

Also, in the case of using the supporting salt, the kinds of the supporting salt are not particularly limited

so long as it can control the electrical conductivity of the aqueous medium without preventing the formation of micelle or the deposition of said pigments on the electrode.

5 Specifically, sulfuric acid salts (salts of lithium, potassium, sodium, rubidium or aluminum), acetic acid salts (salts of lithium, potassium, sodium, rubidium, beryllium, magnesium, calcium, strontium, barium or aluminum), salts of halides (salts of lithium, potassium, sodium, rubidium, calcium, magnesium or aluminum), salts of water-soluble oxides (salts of lithium, potassium, sodium, rubidium, calcium, magnesium or aluminum), which are generally and widely used as supporting salts, are suitable. For example, LiBr, KCl, Li₂SO₄, (NH₄)₂BF₄ and so on can be mentioned.

Then, three kinds of dispersions wherein the red, green and blue pigments are respectively dispersed are prepared. A micelle dispersion comprising a mixed system of pigments can be prepared either by placing all the pigments to be incorporated simultaneously in the aqueous medium along with the surfactants and the supporting salts and dispersing these components or by placing a single pigment to be incorporated in the aqueous medium along with the surfactants and the supporting salt, dispersing these components to prepare a dispersion and mixing the three dispersions thus prepared.

Next, a substrate for manufacture of color filter comprising an electrically insulating substrate and a transparent electroconductive thin film thereon, for example an ITO (a composite oxide comprising indium oxide and tin oxide) substrate with a black matrix or a solid or patterned ITO substrate is dipped into one of the dispersions prepared as above. Said substrate is electrified to be subjected to the micellar electrolysis and the desired film of coloring matter is formed on the electrode of said substrate. This procedure is repeated for each of the remaining two dispersions to form a film of coloring matter in the three primary colors of RGB on said substrate. As the electrically insulating substrate used to prepare said substrate for manufacture of color filter, a glass substrate such as blue plate glass (soda lime), white plate glass, alkali-free glass (for example, 7059, produced by Corning Glass Works; NA 45, produced by HOYA CO., LTD.), low expansion glass (LE), quartz glass and so on and a plastic plate such as polyethylene terephthalate can be mentioned. Of them, the glass plates are suitable. As the glass plate, the polished products are preferable but even the unpolished glass plates can be used. The material of the transparent electroconductive thin film on these electrically insulating substrates is acceptable, provided it is a metal more noble than the oxidation potential of the ferrocene derivatives or an electrically conductive substance. More specifically, an electrically conductive metal oxide such as 40 ITO (a composite oxide comprising indium oxide and tin oxide), tin dioxide and so on and further an electroconductive polymer can be mentioned. The thin films are formed according to, for example the sputtering method, the vapor deposition method, the CVD method, the coating method and so on. Further, it is advantageous to coat silica on a glass plate and then form an electroconductive thin film thereon, to provide improved adhesion between the electroconductive thin film and the glass plate.

As the substrate for manufacture of color filters, an ITO substrate with a black matrix is preferably used. The ITO substrate with black matrix is prepared by forming the black matrix on an electrically insulating

substrate according to the photography method at first. The black matrix formed as above is subjected to patterning according to the photolithography method in the order of: (a) coating of a resisting agent, (b) exposure, (c) developing, (d) postbaking, (e) etching of an electroconductive thin film and (f) removal of the resist. Further, exposure should be carried out by the use of a mask for manufacturing the black matrix.

An electrically insulating film can additionally be laid on the substrate after the black matrix is formed thereon. The electrically insulating films are formed by sputtering silica (SiO_2), titania (TiO_2), alumina (Al_2O_3) and so on or coating or dipping silica or a polymer.

Then, an ITO thin film is formed on said electrically insulating film or glass plate. The ITO thin films can be formed according to the sputtering method, the vapor deposition method, the pyrosol method and so on.

Furthermore, the ITO thin films are patterned according to the photolithography method to form ITO electrodes. These ITO thin films are subjected to the patterning process according to the photolithography method by repeating the same procedure as in patterning of the electrically insulating thin films as set forth above. Moreover, the ITO electrodes are used as an electrode for forming layers of coloring matter, ordinarily having a stripe pattern.

In this way, the substrates for manufacture of color filter having the transparent electroconductive thin film on electrically insulating substrate is prepared.

In the present invention, said substrate for manufacture of color filter is dipped into one of said three dispersions and electrified to be subjected to the micellar electrolysis. The electrolytic conditions are determined depending on various circumstances. Usually, the liquid temperature is 0° to 90° C. and preferably 10° to 40° C., and the voltage is 0.03 to 1.5V and preferably chosen in the range of the oxidation-reduction potential to 0.9V.

Then, the procedure mentioned as above is repeated for each of the remaining two dispersions to obtain the film of coloring matter in the three primary colors of RGB on said substrate.

The micellar electrolytic treatment may as well be carried out according to the following method. On the substrates for manufacture of color filter, the patterned electroconductive thin films are divided into an objective electrode and other electrodes. The objective electrode is impressed with a potential higher than the oxidation-reduction potential of said micelle forming agent. At least one of the other electrodes is impressed with a potential in the range that does not permit the production of films including self potential (control potential). More specifically, control potential is lower than oxidation-reduction potential of said micelle forming agent.

When ferrocene derivatives are used as the micelle forming agent singly, and it is an FPEG, the objective electrode is impressed with potential of approximately +0.3 to +0.9V and the other electrodes are impressed with potential of approximately -0.3 to +0.28V. When it is a FEST8, the objective electrode and the other electrodes are respectively impressed with potential of 0.3 to +0.9V and -0.3 to +0.25V; when it is a FEST9, +0.3 to 0.9V and -0.3 to +0.25V; and when it is a FTMA, +0.2 to +0.9V and -0.3 to +0.20V.

Next, one embodiment of this method will be described below. In the substrates for manufacture of color filter having the R, G and B patterned transparent electrodes, when the film of coloring matter in R is

formed from said red pigment at the R electrode, the R electrode is assigned as the objective electrode and the G and B electrodes as the other electrodes. Then, the dispersion containing said red pigment is subjected to an electrolytic treatment. Next, the G electrode is assigned as the objective electrode and the R and B electrodes as the other objective to electrolyze the dispersion containing said green pigment. Finally the B electrode is assigned as the objective electrode and the R and G electrodes as the other electrodes to electrolyze the dispersion containing said blue pigment, to form the film of coloring matter in the three primary colors of RGB on said substrate.

In this way, the films of coloring matter having a uniform thickness can be obtained according to the micellar disruption method.

In the present invention, the color films produced by this micellar electrolytic treatment are ordinarily rinsed with an electrical conductivity adjusting solution, pure water and an electrolyte. Then, they are dried with warm water and then prebaked at a temperature of approximately room temperature to 140° C. for about 5 to 30 minutes.

The thus produced films of coloring matter in the three primary colors of RGB are ordinarily provided with a protect coat to protect the surface of said color films. The protect coats can be formed by spin coating an acrylic, ester-based, polyimide-based, cyclized rubber-based, siloxane-based or epoxy-based homopolymer or copolymer and so on. Then, an ITO thin film is formed thereon by sputtering ITO according to a conventional method, followed by ITO patterning as directed by a conventional method. Thus, the desired color filters are obtained. Further, ITO sputtering can be replaced by subjecting ITO to the masking vapor deposition to dispense with the procedure for ITO patterning.

Prepared by the micellar electrolytic treatment according to the present invention, the color filters having the film of coloring matter in the three primary colors of RGB are excellent in spectral properties, having improved depolarizing properties. These color filters are also very excellent in heat resistance and light resistance since they are free of binder resins.

Next, the pigment dispersion method for manufacturing color filters, other than the method of the present invention, will briefly be described below.

In said pigment dispersion method, red, green and blue pigments as desired are respectively added to an appropriate organic solvent such as ethyl cellosolve acetate. Then, an acrylic or acrylic/acrylate-based resisting agent and a triazine-based initiator are added thereto. These components are mixed homogeneously by the use of a mixer, and the resultant mixture is subjected to the classification procedure comprising centrifugation and filtration (of Teflon or polypropylene), to prepare three kinds of pigment-dispersed resists of R, G and B. A pigment-dispersed resist comprising a mixed system of pigments can be prepared by either of the following two steps. One of them is to add all the pigments to be mixed to an organic solvent along with a resisting agent and an initiator simultaneously and disperse them. Another is to add a single pigment to be mixed to a organic solvent along with a resisting agent and an initiator, disperse them to obtain a pigment-based resist and mix a plurality of pigment-based resists thus produced.

In said pigment-dispersed resists, it is desired that the primary particles of the organic pigments be adjusted to have an average particle size of 20~200 nm and further a particle size distribution within ± 35 nm. It is also desirable to choose the pigments and adjust their mixing ratio in a manner that the film of coloring matter in green has a ratio (T_{485}/T_{610}) of the transmittance at 485 nm (T_{485}) to that at 610 nm (T_{610}) of 3.5 or less, the maximum transmittance of said film of coloring matter in green is 60% or more and said maximum transmittance is assigned the wavelengths in the range of 540 to 550 nm.

Next, on the substrate for manufacture of color filter, for example the ITO substrate with black matrix, one of said pigment-dispersed resists is coated at a revolution of about 500~3000 rpm by the use of a spin coater or roll coater. The resultant coat is prebaked at a temperature of about room temperature to 150° C. for 5 to 60 minutes and then subjected to exposure by the use of a high-pressure mercury lamp and so on. The substrate is developed, rinsed and postbaked at a temperature of about 150° to 280° C. for about 30 to 150 minutes to form the desired film of coloring matter on said substrate. This procedure is repeated for each of the remaining two pigment-dispersed resists and thus the films of coloring matter in the three primary colors of RGB are prepared on said substrate.

Further on the color films formed as above, the protect coat (top coat) and the ITO thin film are provided and the resultant substrate is subjected to ITO patterning, by repeating the same procedure as in said micellar disruption method. In this way, the desired color filters are obtained.

The color filters of the present invention are excellent in light resistance, and when they are used in liquid crystal projectors, capable of withstanding the use of intensely bright light sources. These color filters are also resistant to the heat generated when the light is irradiated to the color filters from intensely bright light sources. Accordingly, liquid crystal projectors of single plate type using highly bright light sources will be made available with the advent of the color filters of the present invention. The liquid crystal panels for overhead projector and for car can use strong light sources because of the color filters of the present invention, to have higher reliability and a longer life.

As set forth above, the color filters of the present invention are very advantageous to liquid crystal projectors (liquid crystal television projectors, overhead projectors, video projectors and so on). Eventually one object of the present invention is to provide a liquid crystal projector using said color filter.

The present invention will be described in more detail below by the following examples, which are not to be construed as limiting the scope of the invention to their details.

PREPARATION EXAMPLES 1~12:

Preparation of the Dispersion for Micellar Disruption Method

In 5 L (L=liter) of pure water, lithium bromide was placed in a concentration of 0.1 mol/L and further thereto a surfactant comprising FPEG or FEST and a pigment in an amount and ratio listed in Table 1 were mixed with stirring. Under the condition of a liquid temperature at 30° C. ± 5 ° C., the resultant mixture was dispersed for a period of time listed in Table 1 in the presence of ultrasonic waves by the use of a continuous

ultrasonic dispensing device (RUS-600T, 600 W, produced by NIHON Seiki Seisakusho), and then subjected to the treatments listed in Table 1, to prepare a dispersion. The dispersion thus obtained was centrifuged at a revolution and for a period of time as listed in Table 1 by the use of an angle rotor (RPR10-2, produced by Hitachi Koki Co., Ltd.) in a centrifuge (C20B2, produced by Hitachi Koki Co., Ltd.) under the condition of 25° C., to classify the particles of pigments. This centrifuge had a centrifugal force of 12600×g at 9500rpm and 6200×g at 8000rpm. The primary particles of pigment contained in the dispersions formed as above were observed for their particle size distribution by the use of a transmission electron microscope (H-800, produced by Hitachi, Ltd.). The results are given in Table 1 in terms of weight average particle size and the range of particle size distribution with respect to the primary particles.

TABLE 1

Example	C.I. No.	Brandname	Pigment	Surfactant
			concentration (g/l)	concentration (mmol/l) Kind
1	P.R. 168	Monolight Red 2Y ⁴⁾	45.2	9.05 FEST8
2	P.R. 177	Chromophthal Red A2B1)	22.6	4.66 FEST9
3	P.G. 7	Fastgen Green S ³⁾	29.7	5.97 FPEG
4	P.G. 36	Heliogen Green L9361 ²⁾	29.7	5.64 FEST9
5	P.G. 36	Heliogen Green L9361 ²⁾	29.7	5.64 FEST9
6	P.Y. 110	Irugazine Yellow 2RLT ¹⁾	66.0	12.3 FEST9
7	P.Y. 110	Irugazine Yellow 2RLT ¹⁾	66.0	12.3 FEST9
8	P.Y. 83	Similar Fast Yellow 418 ^{1,3)}	33.0	7.68 FEST9
9	P.Y. 83	Similar Fast Yellow 418 ^{1,3)}	33.0	7.68 FEST9
10	P.B. 15:3	Fastgen Blue TGR ³⁾	13.8	2.94 FEST9
11	P.B. 15:6	Fastgen Blue EP-7 ³⁾	55.0	10.7 FPEG
12	P.V. 23	Fastgen Super Violet 2RN ³⁾	9.75	2.34 FEST9
Example			Weight average particle size (nm)	Range of particle size distribution (nm)
1	Ultrasonic wave, 18 hr.: Centrifugation, 9500 rpm, 17.5 min.		82.3	+23.5 ~ -26.8
2	Ultrasonic wave, 18 hr.: Centrifugation, 9500 rpm, 17.5 min.		41.2	+33.8 ~ -26.2
3	Ultrasonic wave, 18 hr.: Centrifugation, 9500 rpm, 17.5 min.		34.3	+28.3 ~ -25.7
4	Ultrasonic wave, 24 hr.: Centrifugation, 8000 rpm, 17.5 min.		22.4	+20.5 ~ -13.3
5	Ultrasonic wave, 24 hr.: No centrifugation		34.2	+66.2 ~ -25.6
6	Ultrasonic wave, 24 hr.: No centrifugation		52.4	+40.2 ~ -36.4
7	Ultrasonic wave, 24 hr.: Centrifugation, 9500 rpm, 35.0 min.		34.8	+29.5 ~ -21.1
8	Ultrasonic wave, 18 hr.: No centrifugation		54.6	+61.8 ~ -45.1
9	Ultrasonic wave, 18 hr.: Centrifugation, 9500 rpm, 35.0 min.		39.45	+34.5 ~ -26.6
10	Ultrasonic wave, 12 hr.: Centrifugation, 9500 rpm,		44.95	+24.9 ~ -34.8

TABLE 1-continued

11	17.5 min. Ultrasonic wave, 18 hr.: Centrifugation, 9500 rpm, 35.0 min.	48.5	+26.9 - 30.2
12	Ultrasonic wave, 12 hr.: Centrifugation, 9500 rpm, 17.5 min.	49.2	+34.1 - 32.6

Note:

- 1)Ciba Geigy Co.
2)BASF Co.
3)DAINIPPON INK & CHEMICALS INC.
4)ICI Co.

PREPARATION EXAMPLES 13~20:

Preparation of Resisting Agent for Dispersion Method

ECA (ethyl cellosolve acetate), a dispersing aid, a sorbitan fatty acid ester compound and a pigment were mixed and dispersed by a sandmill. Then, the mixture was subjected to the treatments listed in Table 2 to prepare a dispersion. The amount of the pigments added is summarized in Table 2. The pressure filtration was carried out by the use of a filter of Teflon having an average pore size of 0.45 μm.

The primary particles of pigment contained in the dispersion formed as above were observed for their particle size distribution by the use of a transmission electron microscope (H-800, produced by Hitachi, Ltd.). The results are given in Table 2 in terms of weight average particle size and the range of particle size distribution with respect to the primary particles of organic pigments. Furthermore, to 1 L of said dispersion, 1 L of a solution of a resin of ultraviolet setting type dissolved in the ECA solvent (CT: produced by Fuji Hunt Electronics Technology Co., Ltd.; concentration of solids of 20% by weight) was added and both of them were mixed sufficiently to prepare a resisting solution.

TABLE 2

Example	Kind of Pigment		Concentration of pigment (g/l)
	C.I. No.	Brandname	
13	P.R. 177	Chromophthal Red A2B ¹⁾	113
14	P.G. 36	Helio Green L9361 ²⁾	149
15	P.Y. 110	Irgazine Yellow 2RLT ¹⁾	165
16	P.Y. 110	Irgazine Yellow 3RLTN ¹⁾	145
17	P.Y. 139	Pariotol Yellow L1820 ²⁾	124
18	P.Y. 139	Pariotol Yellow L1820 ²⁾	124
19	P.B. 15:6	Lionol Blue B-ESS ³⁾	68
20	P.v. 23	Fastgen Super Violet RN ³⁾	48

Example	Treatments	Weight average Particle size (nm)	Range of particle size dist- ribution (nm)
13	Pressure filtration	93.7	+28.3 - 33.7
14	Pressure filtration	45.3	+24.7 - 23.3
15	Pressure filtration	45.2	+29.5 - 19.8
16	No treatment	118.4	+68.2 - 42.5
17	Pressure filtration	58.4	+31.6 - 28.4

TABLE 2-continued

18	No treatment	74.2	+62.3 - 44.3
19	Pressure filtration	60.2	+31.4 - 27.2
20	Pressure filtration	59.9	+31.6 - 26.9

Note:

- 1)Ciba Geigy Co.
2)BASF Co.
3)DAINIPPON INK & CHEMICALS INC.
4)TOYO INK MFG. CO., LTD.

EXAMPLE 1:

Process for Patterning ITO Substrate

On a glass substrate having a face resistance of 20Ω/□ (blue plate glass, polished, silica-dipped material, produced by Geomatec Co., Ltd.), a resisting agent of ultraviolet setting type (FH22130, produced by Fuji Hunt Electronics Technology Co., Ltd.) was spin coated at a revolution of 1000rpm. After spin coating, said resist/ITO substrate was prebaked at 80° C. for 15 minutes, and then, set to an exposer. By the use of a mask for pattern of 1920 strips in length, 100 μm in line width, 20 μm in gap, 230 μm in line length, a high-pressure mercury lamp of 2kW, and with a proximity gap of 70 μm, the substrate was subjected to an exposure at 120 mJ/cm². Then, the substrate was developed with a developer (FHD-5, produced by Fuji Hunt Electronics Technology Co., Ltd.), rinsed with pure water, and postbaked at 180° C. Next, an aqueous solution of 1M FeCl₃·6N HCl·0.1N HNO₃·0.1N Ce(NO₃)₄ was prepared as an etching solution, and ITO of said substrate was subjected to etching with the etching solution. The end point of etching was determined by electric resistance. Said etching took a period of about 20 minutes.

After etching the substrate was rinsed with pure water, and the resist was removed with 1N NaOH.

Thus, ITO patterned glass substrates were prepared.

Process for Forming Black Matrix

Subsequently, as a resisting agent for forming a black matrix, a mixture of CK with CR, CG, and CB of Color Mosaic series (produced, by Fuji Hunt Electronics Technology Co., Ltd.) each in the amount of 3:1:1:1 by weight was used. The ITO patterned glass substrate formed as above was revolved at 10rpm, 30 cc of this resisting agent was sprayed on it, and then the revolution of the spin coater was raised to 500 rpm, to form a uniform film on the substrate. The substrate after spin coating was prebaked at 80° C. for 15 minutes. By the use of a mask designed for black matrix (90×310 μm square, 20 μm in line width), while positioning adjusting with an exposer having a high-pressure mercury lamp of 2 kW and also alignment function, said substrate was subjected to exposure. As the light source, a high-pressure mercury-vapor lamp of 2 kW was used, with a proximity gap of 70 μm, and subjected to exposure at 100mJ/cm². Then, the substrate was developed with an alkali developer. Then, Fuji Hunt CD (a developer) was diluted with pure water 4-fold, and the substrate was developed with the diluent again for 30 seconds, rinsed with pure water and postbaked at 200° C. for 100 minutes.

Process for Preparing Dispersion

As the dispersion of R, the dispersion of Chromophthal Red A 2B (produced, by Ciba Geigy Co., Ltd.) prepared in Preparation Example 2 was used.

Also, as the mixed dispersion of G, the dispersion of Heliogen Green L9361 (produced by BASF Co., Ltd.) prepared in Preparation Example 4 was mixed with the dispersion of Irugazine Yellow-2RLT (produced by Ciba Geigy Co., Ltd.) in a ratio of 70:30 by weight, the mixture was dispersed for 30 minutes by the use of a ultrasonic homogenizer, and the mixture thus homogenized was used.

Further, as the mixed dispersion of B, the dispersion of Fastgen Blue-TGR (produced by DAINIPPON INK & CHEMICALS, INC.) prepared in Preparation Example 10 was mixed with the dispersion of Fastgen Super Violet 2RN (produced by DAINIPPON INK & CHEMICALS, INC.) in a ratio of 80:20 by weight and the resultant mixture was used.

Process for Preparing Film of Coloring Matter

Into said dispersion of R, said ITO patterned substrate was dipped, and a potentiostat was connected to line R of the stripe, subjected to a constant potential electrolysis of 0.5V vs. SCE, for 25 minutes, to obtain a thin film of color filter R. The thin film was washed with pure water, and baked in an oven at 100° C. for 15 minutes.

Next, this substrate was dipped into said dispersion of G, and subjected to a constant potential electrolysis of 0.5V vs. SCE, for 20 minutes, to obtain a thin film of color filter RG. After film forming, the thin film was subjected to the after treatment under the same conditions as in R.

Lastly, this substrate was dipped into said dispersion of B and subjected to a constant potential electrolysis of 0.5V vs. SCE, for 15 minutes, to obtain a thin film of color filter RGB. The thin film was subjected to the after treatment under the same conditions as in R. Thus, color filter films of RGB were prepared.

Formation of Protect Coat

Said substrate with the color film thereon was set to a spin coater, and OS-808 (produced by NAGASE & CO., LTD.) as a top coating agent was sprayed on it by the use of a dispenser. Thereupon, the substrate was slowly revolved at 10 rpm, to coat evenly all over the substrate. Then, the revolution was raised and the substrate was revolved at 800 rpm for 2 minutes to obtain a uniform thin film. The thin film was postbaked at 260° C. for 2 hours and cured. Thus, color filters RGB having protect coat were prepared.

Results of Evaluation

(1) Evaluation of Light Resistance

This color filter was broken into about 5cm-long pieces, and one piece of them was used to determine chromaticity coordinates for each color of RGB and spectral properties (FIG. 1) of said piece were measured according to TC-1800DAM (produced by Tokyo Denshoku Co., Ltd.). Then, the light was irradiated to this piece of the color filter at a illuminance of 1,000,000 lux for 100 hours by the use of a metal halide lamp of 160 W. Thereon, the surface temperature was found to be 30° C.

The results are given in Table 3. It was found that the color difference ΔEab of each color of RGB remained

almost unchanged before and after the irradiation of the light. The color difference determined according to TC-1800DAM (produced by Tokyo Denshoku Co., Ltd.) is expressed in terms of ΔEab of the Lab system (JIS Z-8730).

(2) Evaluation of Depolarizing Properties

Two polarizers running side by side were turned around to proceed one polarized light in the direction forming an angle of 90° with the direction of another polarized light, and the ratio of brightness before and after the turnabout (contrast) was found to be 2000. Next, another piece of the color filter was placed between these two polarizers. The polarizers were likewise turned around to proceed the two polarized lights in the directions forming an angle of 90° one another and the ratio of brightness before and after the turnaround were determined. As the result, it was found that, among RGB, R had the lowest ratio of brightness of 909, to mark a striking contrast as compared with conventional color filters.

EXAMPLE 2:

Formation of Black Matrix

On an alkali-free glass substrate (NA45/300 square, 1.1 mm thick, produced by HOYA Co., Ltd.), Cr was sputtered to form a Cr thin film of about 2000A (SDP-550VT, produced by Alback Co., Ltd.). Further on it, a resisting agent of positive type (FH-2130, produced by Fuji Hunt Electronics Technology Co., Ltd.) was spin coated at a revolution of 1000 rpm. After spin coating, this resist/Cr/glass substrate was prebaked at 80° C. for 15 minutes and then set to a stepper exposer. By the use of a mask for picture element of 90 μm × 310 μm, 20 μm in line width and a quarter of grill pattern having an effective area of 160 mm × 155 mm, the substrate was subjected to an exposure at an exposure capacity of 100mJ/cm² and an scanning speed of 5 mm/second. Then, the substrate was developed with an exclusive developer, rinsed with pure water and postbaked at 150° C. Next, an aqueous solution of 1N HClO₄·0.1N HNO₃·0.1N Ce(NO₃)₄ was prepared as an etching solution, and Cr of said substrate was subjected to etching with the etching solution. The end point of etching was determined by electric resistance. Said etching took a period of 20 minutes. After etching, the substrate was rinsed with pure water, and the resist was removed with 1N NaOH. Said substrate was rinsed well with pure water, and thus black matrixes (BM) were prepared.

Formation of Electrically Insulating Film and ITO Thin Film Electrode

Subsequently, on this BM, OCD TYPE-7 (silica, produced by Tokyo Ohka Kogyo Co., Ltd.) was spin coated as an electrically insulating film at a revolution of 1000 rpm, baked at 250° C. for 60 minutes and cooled to room temperature. Then, the substrate was set to SDP-500VT (produced by ULVAC Co., Ltd.), and ITO was sputtered from above the substrate to form an ITO film of about 1700 Å. Thereon, the ITO was adjusted to have a surface resistance of 20Ω/□ at a work temperature of 180° C. On this ITO film/Cr/glass substrate (NA45, 300 square, produced by HOYA Co., Ltd.), a resisting agent of positive type (FH-2130, produced by Fuji Hunt Electronics Technology Co., Ltd.) was spin coated at a revolution of 1000 rpm. After spin coating, this resist/ITO/Cr/glass substrate was pre-

baked at 80° C. for 15 minutes and set to a contact exposer. By the use of a mask for stripe pattern in length of 92 μm in line width, 18 μm in gap, 155 mm in line length, a high-pressure mercury lamp of 2 kW and while aligning, and with a proximity gap of 50 μm , the substrate was subjected to an exposure at 120mJ/cm². Then, said substrate was developed with 2.1 wt % of TMAH (tetramethyl ammonium hydride) as an alkali developer, rinsed with pure water and postbaked at 150° C. Next, an aqueous solution of 1M FeCl₃.1N HCl.0.1N HNO₃.0.1N Ce(NO₃)₄ was prepared as an etching solution, and ITO of said substrate was subjected to etching with the etching solution. Said etching took a period of 20 minutes. After etching, the substrate was rinsed with pure water and the resist was removed with 1N NaOH. Then, said substrate was rinsed with pure water, and no electrical leak was confirmed between two adjacent ITO electrodes. Thus, substrates with ITO patterned BM were prepared.

Formation of Taken-out Electrode Mounting

As a taken-out electrode mounting, an acrylic resisting agent (CT, produced by Fuji Hunt Electronics Technology Co., Ltd.) was used.

The substrate having an ITO patterned BM as obtained in the preceding process was revolved at 10 rpm, 30 cc of said resisting agent was sprayed on it and the revolution of the spin coater was raised to 1500 rpm to form a uniform film on the substrate. This substrate was prebaked at 80° C. for 15 minutes. By the use of a mask designed to prepare only parts of taken-out electrode mounting (see FIG. 5), while positioning with a contact exposer having a high-pressure mercury lamp of 2 kW and also alignment function, said substrate was subjected to an exposure. Then, the substrate was developed with a developer for 90 minutes, rinsed with pure water and postbaked at 180° C. for 100 minutes. Thus, substrates for manufacturing color filters were completed.

Process for Preparing Dispersion

As the mixed dispersion of R, the dispersion of Chromophthal Red A 2B (produced by Ciba Geigy Co.) prepared in Preparation Example 2 was mixed with the dispersion of Irugazine Yellow 2RLT (produced by Ciba Geigy Co.) prepared in Preparation Example 7 in a ratio of 65:35 by weight, and the resultant mixture was dispersed for 30 minutes by the use of a ultrasonic homogenizer. Thus, the mixed dispersion of R formed as above was used.

Also, as the mixed dispersion of G, the dispersion of Heliogen Green L9361 (produced by BASF Co.) prepared in Preparation Example 4 was mixed with the dispersion of Irugazine Yellow 2RLT (produced by Ciba Geigy Co.) prepared in Preparation Example 7 in a ratio of 70:30 by weight, and the resultant mixture was dispersed for 30 minutes by the use of a ultrasonic homogenizer, and thus, the mixed dispersion of G formed as above was used.

Furthermore, as the mixed dispersion of B, the dispersion of Fastgen Blue TGR (produced by DAINIPPON INK & CHEMICALS, INC.) prepared in Preparation Example 10 was mixed with the dispersion of Fastgen Superviolet 2 RN (produced by DAINIPPON INK & CHEMICALS, INC.) prepared in Preparation Example 12 in a ratio of 80:20 by weight, and thus, the mixture of B formed as above was used.

Process for Preparing Film of Coloring Matter

Into said dispersion of R, said patterned ITO substrate was dipped, and a potentiostat was connected to line R of the stripe, subjected to a constant potential electrolysis of 0.5V vs. SCE for 25 minutes, to obtain a thin film of color filter R. The thin film was washed with pure water and baked in an oven at 100° C. for 15 minutes.

Next, this substrate was dipped into said dispersion of G and subjected to a constant potential electrolysis of 0.5V vs. SCE for 20 minutes, to obtain a thin film of color filter RG. Then, the thin film was subjected to the after treatment under the same conditions as in R.

Lastly, this substrate was dipped into said dispersion of B and subjected to a constant potential electrolysis of 0.5V vs. SCE for 15 minutes to obtain a thin film of color filter RGB. Then, the thin film was subjected to the after treatment under the same conditions as in R.

Thus, color thin films of color filter RGB were prepared.

Formation of Protect Coat

Subsequently, the RGB color filter substrate formed as above was revolved at 10 rpm, 30 cc of SS-7265 (produced by Japan Synthetic Rubber Co., Ltd.) as a topcoating agent was sprayed on it and the revolution of the spin coater was raised to 1000 rpm to obtain a uniform film on the substrate (the color thin film of RGB color filter). Then, this thin film was postbaked at 220° C. for 50 minutes.

Result of Evaluation

The result of evaluation conducted in the same manner as Example 1 is shown in Table 3.

EXAMPLE 3 AND COMPARATIVE EXAMPLE 1:

The color filter was prepared in the same manner as in Example 2 except that the pigment dispersions prepared as listed in Table 3 were used in place of the micellar electrolytes of RGB. The result is shown in Table 3.

TABLE 3

	Preparation Example (Mixing Ratio by Weight)			
	R	G	B	
Example 1	2 (100)	4/7(70:30)	10/12(80:20)	
Example 2	2/7(65:35)	4/7(70:30)	10/12(80:20)	
Example 3	1/7(65:35)	3/7(70:30)	10/12(80:20)	
Comp.	2/7(65,35)	5/6(85:15)	10/12(80:20)	
Example 1				
Color difference ΔE_{ab} (before/after)				
	R	G	B	
Example 1	0.7	1.2	1.1	909
Example 2	1.1	0.6	1.3	1111
Example 3	1.0	0.9	1.3	930
Comp.	1.2	22.5	1.3	—
Example 1				

EXAMPLE 4:

Formation of Black Matrix

On an alkali-free glass substrate (NA 45/300 square, 1.1 mm thick, produced by HOYA Co., Ltd.), Cr was sputtered to form a Cr thin film of about 2000A (SDP-550VT, produced by ULVAC Co.), and further thereon a resisting agent of positive type (FH-2130, produced by Fuji Hunt Electronics Technology Co.,

Ltd.) was spin coated at a revolution of 1000 rpm. After spin coating, said resist/Cr/glass substrate was pre-baked at 80° C. for 15 minutes and then set to a stepper 10 exposer. By the use of a mask for picture element of 90 $\mu\text{m} \times 310 \mu\text{m}$, 20 μm in line width, a quarter of grill pattern having an effective area of 160 mm \times 155 mm, said substrate was subjected to exposure of i-line. The exposure was carried out at a scanning speed of 5 mm/second and at an exposure capacity of 120 mJ/ cm^2 and then the substrate was developed with 10 an exclusive developer. After being developed, said substrate was rinsed with pure water and postbaked at 150° C. Subsequently, an aqueous solution of 1N HClO₄-0.1N HNO₃-0.1N Ce(NO₃)₄ was prepared as an etching solution, and Cr of said substrate was etched with the etching solution. Said etching took a period of 20 minutes. After etching, the substrate was rinsed with pure water, and the resist was removed with 1N NaOH. Said substrate was rinsed well with pure water, and thus black matrixes (BM) were completed.

Formation of electrically insulating Film

Next, on this BM, CCD TYPE-7 (silica, produced by Tokyo Ohka Kogyo Co., Ltd.) was spin coated as an electrically insulating film at a revolution of 1000 rpm.

This electrically insulating film was baked at 250° C. for 60 minutes and cooled to room temperature.

Process for Preparing Pigment-dispersed Resist and Forming Film

Said substrate having a CrBM was revolved at 10 rpm, 30 cc of the resisting agent of R prepared in Preparation Example 13 was sprayed on it and then the revolution of the spin coater was raised to 500 rpm to form a uniform film on the substrate. The substrate was pre-baked at 80° C. for 15 minutes. By the use of a mask designed for stripe of R, while positioning with an exposer having a high-pressure mercury lamp of 2 kW and also alignment function, said substrate was subjected to exposure. Then, the substrate was developed for 30 seconds with a developer which was prepared by diluting the Fuji Hunt CD (a developer) with pure water 4-fold, rinsed with pure water and postbaked at 200° C. for 100 minutes.

Next, the dispersion of Preparation Example 14 was 45 mixed with the dispersion of Preparation of Example 15 in a ratio of 7:3 by weight to prepare the resisting agent of G. Said BM substrate having the R resist as formed above was revolved at 10 rpm, 30 cc of the resisting agent of G was sprayed on it and then the revolution of 50 the spin coater was raised to 500 rpm to form a uniform film on the substrate. The substrate was prebaked at 80° C. for 15 minutes. By the use of a mask designed for stripe of G, while positioning with an exposer having a high-pressure mercury lamp of 2 kW and also alignment function, said substrate was subjected to exposure. Then, the substrate was developed for 30 seconds with a developer which was prepared by diluting the Fuji Hunt CD (a developer) with pure water 4-fold, rinsed with pure water and postbaked at 200° C. for 100 minutes.

Subsequently, the dispersion of Preparation Example 19 was mixed with the dispersion of Preparation Example 20 in a ratio of 9:1 by weight to prepare a resisting agent of B. Said BM substrate having the RG resists as 65 formed above was revolved at 10 rpm, 30 cc of the resisting agent of B was sprayed on it and then the revolution of spin coater was raised to 500 rpm to form

a uniform film on the substrate. The substrate was pre-baked at 80° C. for 15 minutes. By the use of a mask designed for stripe of B, while positioning with an exposer having a high-pressure mercury lamp of 2 kW and also alignment function, said substrate was subjected to exposure. Then, the substrate was developed for 30 seconds with a developer which was prepared by diluting the Fuji Hunt CD (a developer) with pure water 4-fold, rinsed with pure water and postbaked at 200° C. for 100 minutes.

In this way, color filter thin films of RGB were prepared.

Formation of Protect Coat

Next, the RGB color filter substrate formed as above was revolved at 10 rpm, 30 cc of JSS-715 (produced by Japan Synthetic Rubber Co., Ltd.) as a topcoating agent was sprayed on it and the revolution of the spin coater was raised to 1000 rpm to form a uniform film on the substrate (the RGB color thin film of color filter).

Then, the thin film was postbaked at 220° C. for 90 minutes.

Result of Evaluation

The result of evaluation conducted in the same manner as Example 1 is shown in Table 4.

Comparative Example 2

The color filter was prepared in the same manner as in Example 4 except that pigment-dispersed resists prepared as listed in Table 4 were used in place of the pigment-dispersed resist of Example 4. The results are shown in Table 4. Further, the chromaticity coordinates before (solid line) and after (dotted line) the irradiation of light are shown in FIG. 2.

TABLE 4

	Preparation Example (Mixing Ratio by Weight)			
	R	G	B	
Example 4	13 (100)	14/15 (70:30)	19/20 (90:10)	
Comp.	13 (100)	14/18 (70:30)	19/20 (90:10)	
Example 2				
Color difference ΔE_{ab} (before/after)				
	R	G	B	
Example 4	0.9	1.1	3.0	526
Comp.	1.0	39.4	2.9	432
Example 2				
	R	G	B	Contrast

These results clearly demonstrate that, as the kinds of organic pigments and their combinations, it is effective to use the single C.I.P.R. 168, the single C.I.P.R. 177, the mixed system pigment combining C.I.P.R. 168 with C.I.P.Y. 110 or the mixed system pigment combining C.I.P.R. 177 with C.I.P.Y. 110 for red (R); the mixed system pigment combining C.I.P.G.7 or C.I.P.G.36 with C.I.P.Y. 110 for green (G); and the mixed system pigment combining C.I.P.B. 15:3 or 15:4 or 15:6 with C.I.P.V. 23 for blue (B). Examples 5~8:

To produce the color filter in green, the dispersions of Preparation Example 4 and Preparation Example 7 were mixed under the conditions listed in Table 5, to prepare a dispersion. Into this dispersion, a transparent electrode substrate having a face resistance of $20\Omega/\square$ (a 1.1t thick, blue plate glass, produced by Diomatech Co.) as an ITO fill was dipped, and a platinum electrode was used as the counter electrode, subjected to a film-forming treatment for 15 minutes at a potential of 0.5V vs. SEE, to form a fill of coloring matter. This color fill

substrate was washed well with pure water and dried. Said substrate was revolved at 10 rpm, 30 cc of SS-7265 (produced by Nippon Synthetic Rubber Co., Ltd.) as a topcoating agent was sprayed on it and the revolution of the spin coater was raised to 1000 rpm, to obtain a uniform coat on the thin film substrate. The resultant substrate was postbaked at 220° C. for 50 minutes.

The thin film substrate thus produced was determined for its the ratio (T_{485}/T_{610}) of the transmittance of 485 nm (T_{485}) to that of 610 nm (T_{610}), the maximum transmittance (T_{MAX}) of the color fill and the wavelength ascribed to said maximum transmittance (λ_{MAX}). The results are shown in FIG. 5.

It was found that the transmitted light at 485 nm or shorter was shielded by the shielding capability of yellow pigments and the transmitted light at 610 nm or longer was shielded by the shielding capability of green pigments and thus that the ratio of transmittance of 485 nm to that of 610 nm was controlled to be 3.5 or less.

It was also found that the green had the maximum transmittance of 60% or more and that the maximum transmittance of the green was assigned the wavelengths in the range of 540 to 550 nm (λ_{MAX}). Thus, color films in green having ideal spectral properties can be obtained by choosing the appropriate pigments, adjusting their mixing ratios and classifying their particles.

TABLE 5

	Preparation Example (Mixing Ratio by Weight)	T_{485}	T_{610}
Example 5	4/7 (50:50)	8.9	15.9
Example 6	4/7 (60:40)	7.9	12.6
Example 7	4/7 (70:30)	15.1	5.1
Example 8	4/7 (75:25)	17.1	4.9
	T_{485}/T_{610}	T_{MAX} (%)	λ_{MAX} (nm)
Example 5	0.56	77	548
Example 6	0.67	78	545
Example 7	2.96	79	543
Example 8	3.45	79	540

EXAMPLES 9, 10 AND COMPARATIVE EXAMPLES 3~6

Into the micellar electrolytic dispersion listed in Table 6, a transparent electrode substrate having a face resistance of $20\Omega/\square$ (a 1.1 t thick, blue plate glass, produced by Geomatec Co., Ltd.) as an ITO film was dipped, and a platinum electrode was used as the counter electrode, subjected to a film-forming treatment for a period of time listed in Table 6 at a potential of 0.5V vs. SCE, to form a film of coloring matter. The dispersions used as above were found to have the particle size distribution whose typical examples are shown in FIG. 3A (Preparation Example 6) and FIG. 3B (Preparation Example 7).

The color film substrate formed as above was washed well with pure water and dried. Light resistance of the color film substrates thus produced was determined by using a xenon lamp of 13.5 kW and placing a substrate at a distance of 300 mm from the light source. Under the condition of substrate temperature at 70° C., said substrate was subjected to exposure for 100 hours at a visible illuminance of 330,000 lux and at a ultraviolet illuminance of 130 W/m^2 (300 to 400 nm), to determine the color difference before and after the exposure. The results are shown in Table 6.

Where there was high transparency of color films because of the primary particles of pigment having an

average particle size of 20 to 200 nm, said color films could have markedly improved light resistance by controlling the particle size distribution to be within ± 35 nm to obtain uniform particles.

TABLE 6

	Preparation Example (Mixing ratio by weight)	Film- forming time (min.)	Color difference ΔE_{ab} (before/ after)
Comparative	9	2	24.6
Example 3			
Comparative	8	3	37.3
Example 4			
Example 9	7	20	4.3
Comparative	6	15	8.6
Example 5			
Example 10	4/7 (70:30)	20	1.7
Comparative	4/7 (82.5:17.5)	25	5.6
Example 6			

EXAMPLES 11, 12 AND COMPARATIVE EXAMPLES 7~10

Into the micellar electrolytic dispersion listed in Table 7, a transparent electrode substrate having a face resistance of $20\Omega/\square$ (a 1.1 t thick, blue plate glass, produced by Geomatec Co., Ltd.) as an ITO film was dipped, and a platinum electrode was used as the counter electrode, subjected to a film-forming treatment for a period of time listed in Table 7 at a potential of 0.5V vs. SCE, to form a film of coloring matter. This color film substrate was washed well with pure water and dried.

Said substrate was revolved at 10 rpm, 30 cc of SS-7265 (produced by Japan Synthetic Rubber Co., Ltd.) as a topcoating agent was sprayed on it and the revolution of the spin coater was raised to 1000 rpm, to form a uniform coat on the thin film substrate. The resultant substrate was postbaked at 220° C. for 50 minutes.

Light resistance of the color film substrates thus produced was determined by using a xenon lamp of 2.5 kW and placing a substrate at a distance of 90 mm from the light source. Under the condition of substrate temperature at 120° C., said substrate was subjected to exposure for 200 hours at a visible illuminance of 520,000 lux and at a ultraviolet illuminance of 170 W/m^2 (300~400 nm), to determine the color difference before and after the exposure. The results are shown in Table 7.

Where there was high transparency of the color films because of the primary particles of pigment having an average particle size of 20 to 200 nm, said color films could have markedly improved light resistance by controlling the particle size distribution to be within ± 35 nm to obtain the uniform particles.

FIG. 4 shows the spectral transmittance of color films before (solid line) and after (dotted line) the irradiation of light with respect to Example 11(A) and Comparative Example 9(B).

EXAMPLE 13 AND COMPARATIVE EXAMPLE 11

A transparent glass substrate (a 1.1 t thick, blue plate glass, produced by Diomatech Co.) was revolved at 10 rpm, 30 cc of a pigment-dispersed resist listed in Table 7 was sprayed on it and the revolution of spin coater was raised to 1000 rpm, to form a uniform coat on the thin film substrate. The resultant substrate was postbaked at 220° C. for 50 minutes.

Light resistance of the color film substrates thus produced was determined by using a xenon lamp of 2.5 kW and placing a substrate at a distance of 90 mm from the light source. Under the condition of substrate temperature at 120° C., said substrate was subjected to exposure for 200 hours at a visible illuminance of 520,000 lux (380 to 780 nm) and at a ultraviolet illuminance of 70 W/m² (300 to 400 nm), to determine the color difference before and after the exposure. The results are shown in Table 7.

Where there was high transparency of the color films because of the primary particles of pigment having an average particle size of 20 to 200 nm, said color films could have markedly improved light resistance by controlling the particle size distribution to be within ±35 nm to obtain the uniform particles.

TABLE 7

	Preparation Example (Mixing ratio by weight)	Film-forming time (min.)	Color difference ΔE _{ab} (before/ after)
Comparative	9	2	55.5
Example 7			
Comparative	8	3	26.3
Example 8			
Example 11	7	20	2.3
Comparative	6	15	14.8
Example 9			
Example 12	4/7 (70:30)	20	3.7
Comparative	5/6 (82.5:17.5)	25	13.5
Example 10			
Example 13	17	—	3.1
Comparative	18	—	6.4
Example 11			

EXAMPLES 14, 15 AND COMPARATIVE EXAMPLES 12~15

Into the micellar electrolytic dispersion of the Preparation Examples listed in Table 8, a transparent electrode substrate having a face resistance of 20Ω/□ (a 1.1 t thick, blue plate glass, produced by Geomatec Co., Ltd.) as an ITO film was dipped, and a platinum electrode was used as the counter electrode, subjected to a film-forming treatment for a period of time listed in Table 8 at a potential of 0.5 V vs. SCE, to form a film of coloring matter. This color film substrate was washed well with pure water and dried.

Said substrate was revolved at 10 rpm, 30 cc of SS-7265 (produced by Japan Synthetic Rubber Co., Ltd.) as a topcoating agent was sprayed on it and the revolution of the spin coater was raised to 1000 rpm, to form a uniform coat on the thin film substrate. The resultant substrate was postbaked at 220° C. for 50 minutes.

Light resistance of the substrates thus produced was determined by using a metal halide lamp of 160 W and placing a substrate at a distance from the light source to obtain the following illuminance. Under the condition of substrate temperature at 70° C., said substrate was subjected to exposure for 500 hours at a visible illuminance of 1,000,000 lux, to determine the color difference before and after the exposure. The results are shown in Table 8.

Where there was high transparency of the color films because of the primary particles of pigment having an average particle size of 20 to 200 nm, said color films could have markedly improved light resistance by controlling the particle size distribution to be within ±35 nm to obtain the uniform particles.

TABLE 8

	Preparation Example (Mixing ratio by weight)	Film-forming time (min.)	Color difference ΔE _{ab} (before/ after)
Comparative	9	2	54.5
Example 12			
Comparative	8	3	56.2
Example 13			
Example 14	7	20	1.5
Comparative	6	15	8.9
Example 14			
Example 15	4/7 (70:30)	20	2.4
Comparative	5/6 (82.5:17.5)	25	7.1
Example 15			

EXAMPLE 16 AND COMPARATIVE EXAMPLES 16~18

A transparent glass substrate (a 1.1 t thick, blue plate glass, produced by Geomatec Co., Ltd.) was revolved at 10 rpm, 30 cc of a pigment-dispersed resist listed in Table 9 was sprayed on it and the revolution of the spin coater was raised to 1000 rpm, to form a uniform coat on the thin film substrate. The resultant substrate was postbaked at 220° C. for 50 minutes.

Light resistance of the color film substrates thus produced was determined by using a metal halide lamp of 160 W and placing a substrate at a distance from the light source to obtain following illuminance. Under the condition of substrate temperature at 70° C., said substrate was subjected to exposure for 500 hours at a visible illuminance of 1,000,000 lux, to determine the color difference before and after the exposure. The results are shown in Table 9.

Where there was high transparency of the color films because of the primary particles of pigment having an average particle size of 20 to 200 nm, said color films could have markedly improved light resistance by controlling the particle size distribution to be within ±35 nm to obtain uniform particles.

TABLE 9

	Preparation Examples	Color difference ΔE _{ab} (before/ after)
Example 16	15	1.8
Comparative	16	6.1
Example 16		
Comparative	17	7.6
Example 17		
Comparative	18	21.3
Example 18		

EXAMPLE 17

Preparation of Color Liquid Crystal Display

On the surface of a color film substrate having a protect co prepared in Example 2, ITO was subjected to masking vapor deposition to form an ITO film. At this step, the substrate temperature was maintained at 250° C. to obtain an ITO film of 1100Å having a face resistance of 20Ω/□, and thus, color filters were obtained. On the surface of this color filter substrate, a polyamic acid resin monomer was spin coated by repeating the same procedure as in the resists. Then, said resin monomer was cured at 250° C. for 1 hour into polyimide resin, and was subjected to rubbing. After rubbing, between this resin-coated color filter and the above-

mentioned color filter, glass beads and TN liquid crystal were put in in this order, sealed with an adhesive, to complete the panel. After a taken-out electrode mounting a driver IC was connected to FPC, and polarizers were adhesively bonded to both the surfaces, TFT was made to work, to confirm good liquid crystal drive.

The panel formed as above was set to a light source comprising an optical lens having the capacity of 1,000,000 lux, to project by the use of a 100 inch screen. Images were projected for 1000 hours, and then each picture element was determined for its color purity, with the results that R was 92% initially and 92% after projection; G was 70% initially and 69% after projection; and B was 79% initially and 79% after projection. Thus, color deterioration was hardly observed.

Industrial Applicability

The present invention provides the color filters having color films in the three primary colors of RGB, capable of withstanding the use of highly bright light sources and further excellent in light resistance and heat resistance. Particularly, being manufactured according to the micellar disruption method, these color filters are excellent in spectral properties and depolarizing properties, and further superior in light resistance and heat resistance as they are free of binder resins.

With their excellent light resistance, when used in liquid crystal projectors, the color filters of the present invention will enable said liquid crystal projectors to withstand the use of strong light sources. Liquid crystal projectors of single plate type which are resistant to the heat generated when intensely bright light sources are applied to color filters will also come true with the color filters of the present invention. When the color filters of the present invention are incorporated into them, overhead projectors and internal liquid crystal panels for car will be capable of using strong light sources to have marked improvement in reliability and in the life span.

The color filters of the present invention can find good applications in, for example, color FLC liquid crystal panels, color personal computers of lap top type, color word processors, color work stations, color aurora visions, liquid crystal color projectors, liquid crystal color television sets, liquid crystal color OHPs, color internal panels for car, color device monitoring apparatuses and so forth. Eventually the color filters of the

present invention are applicable to and highly useful in a very wide segments of industry.

We claim:

1. A color filter having a film of coloring matter in the three primary colors of red, green and blue which comprises organic pigments to form the film of coloring matter in each of red, green and blue which pigments are comprised of primary particles having an average particle size of 20 to 200 nm and a particle size distribution within +35 nm, and have a color difference of 5 or less when said organic pigments as contained in said color filter are subjected to exposure for 100 hours or more at an illuminance of 100,000 lux or more by the use of a highly bright light source for projection under the condition of a surface temperature at 50° C. or higher.
2. A color filter having films of coloring matter comprising organic pigments in each of the three primary colors of red, green and blue, wherein the color film in green has a ratio (T_{485}/T_{610}) of the transmittance of 485 nm (T_{485}) to that of 610 nm (T_{610}) of 3.5 or less, the maximum transmittance (T_{MAX}) of the film of coloring matter in green is 60% or more and said maximum transmittance is assigned the wavelengths in a range of 540 to 500 nm (λ_{MAX}).
3. The color filter as defined in claim 1 or 2, wherein C.I. Pigment Yellow 110 is used as a yellow pigment to adjust the color tone of either or both of red and green of the organic pigments.
4. The color filter as defined in claim 2, wherein a mixture of C.I. Pigment Yellow 110 and C.I. Pigment Green 36 is used as a pigment to adjust the color tone of at least green of the organic pigments.
5. The color filter as defined in claim 1 or claim 2 having a film of coloring matter in the three primary colors of red, green and blue which comprises a red (R) coloring matter comprising a single P.I. Pigment Red 168 or a single C.I. Pigment Red 177 or a mixed system pigment combining C.I. Pigment Red 168 with C.I. Pigment Yellow 110 or a mixed system pigment combining C.I. Pigment Red 177 with C.I. Pigment Yellow 110; a green (G) coloring matter comprising a mixed system pigment combining at least one compound selected from the group consisting of C.I. Pigment Green 7 and C.I. Pigment Green 36 with C.I. Pigment Yellow 110; and a blue (B) coloring matter comprising a mixed system pigment combining at least one compound selected from the group consisting of C.I. Pigment Blue 15:3, 15:4 and 15:6 with C.I. Pigment Violet 23.

* * * * *



US005176971A

United States Patent [19]

Shimamura et al.

[11] Patent Number: 5,176,971

[45] Date of Patent: Jan. 5, 1993

[54] COLOR FILTER

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[21] Appl. No.: 742,457

[22] Filed: Aug. 5, 1991

Related U.S. Application Data

[60] Continuation of Ser. No. 323,289, Mar. 14, 1991, abandoned, which is a division of Ser. No. 921,047, Sep. 19, 1986, Pat. No. 4,837,098.

[30] Foreign Application Priority Data

Feb. 5, 1985 [JP] Japan 60-20731
Feb. 5, 1985 [JP] Japan 60-20732

[51] Int. Cl. G03F 9/00

[52] U.S. Cl. 430/7; 430/321;
430/13; 430/14; 430/15

[58] Field of Search 430/7, 321, 13, 14,
430/15

[56] References Cited**U.S. PATENT DOCUMENTS**

4,876,165 10/1989 Brewer et al. 430/7

FOREIGN PATENT DOCUMENTS

4012 1/1982 Japan 430/7
201319 9/1984 Japan
237403 10/1985 Japan 430/7

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[57] ABSTRACT

A technique related to color filters to be arranged on the light-receiving surface of a color liquid crystal display device, color video camera, and the like. The color filter consists of a substrate (10) and a colored filter layer (12) formed thereon. The colored filter layer (12) comprises, for example, three groups of filter picture elements (14R), (14G), (14B) having spectral characteristics respectively corresponding to red, green and blue. Each group of filter picture elements are made of polyimide resin and dye contained therein. Further, each group of the filter picture elements (R, G, B) are arranged in direct contact with one surface of the substrate (10) without using any intermediate protecting film. The first group of filter picture elements patterned on one surface of the substrate (10) are subjected to heat treatment at a high temperature of about 250° C., for example, to increase their resistance against the solvent. Then, a second coating layer for patterning the second group of filter picture elements is directly formed without using any intermediate protecting film.

13 Claims, 2 Drawing Sheets

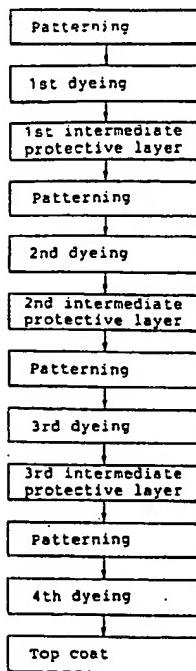


FIG. 1

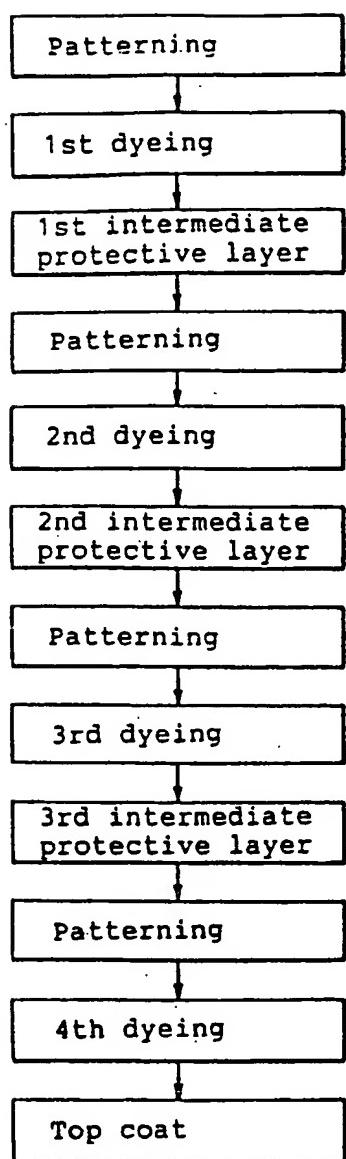


FIG. 2

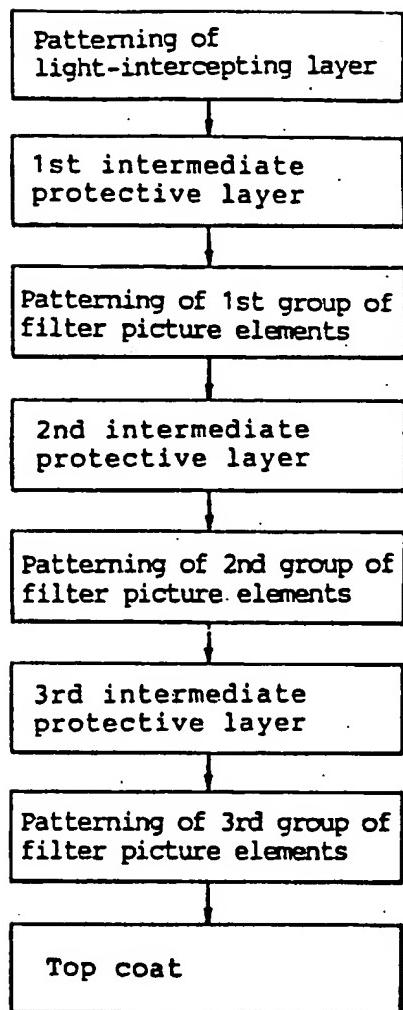


FIG. 3

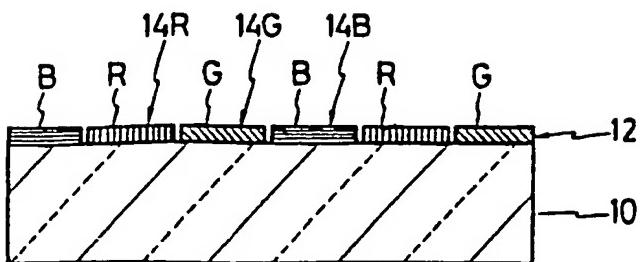


FIG. 4

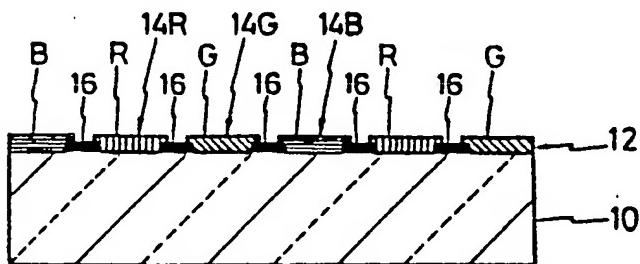
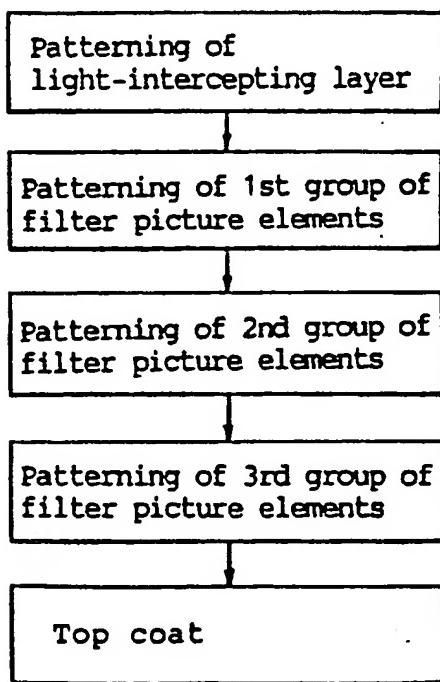


FIG. 5



COLOR FILTER

This is a continuation of copending application(s) Ser. No. 07/323,289 filed on Mar. 14, 1991, now abandoned, which is a division of 06/921,047, filed on Sept. 19, 1986, now U.S. Pat. No. 4,837,098.

FIELD OF THE INVENTION

This invention relates to a color filter adapted to be arranged on a light-receiving surface in a color LCD device, a color video camera or the like, and more particularly to a color filter employing a polyimide having various excellent resistances such as thermal resistance, chemical resistance and light resistance. The invention also relates to a method of producing such a color filter.

PRIOR ART

A color filter of this type comprises a substrate such as a light-transmitting glass plate, and a color filter layer formed on one surface of the substrate. The color filter layer has not less than two groups of filter picture elements which are different in spectral characteristics from each other, and generally has three groups of filter picture elements corresponding respectively to red, green and blue. Each group has a number of filter picture elements having a fine pattern such as a mosaic pattern and a stripe pattern.

It is already known to use polyimide for forming the color filter. For example, Japanese Patent Application Laid-Open No. 58-46326 discloses a technique of coating each group of filter picture elements with polyimide. Japanese Patent Application Laid Open No. 59-29225 discloses a method of forming groups of filter picture elements to form a color filter layer in which after a polyimide layer is subjected to patterning, the groups of filter picture elements thus patterned are dyed in predetermined colors.

FIG. 1 shows a flow chart of a method of producing a color filter using the latter technique which color filter has three groups of filter picture elements corresponding respectively to red, green and blue and light-intercepting layers of a black color each disposed at a boundary between each adjacent filter picture elements. As shown in this Figure, with the conventional technique using dye requires, dying steps and patterning steps are carried out separately, and therefore this method has an increased number of steps and is complicated. In addition, since the polyimide layer subjected to patterning is at least in a semi-cured condition, it is difficult to disperse the coloring material uniformly and sufficiently into the polyimide layer. Thus, this method has such disadvantages.

To overcome the above disadvantages, the inventors of the present invention have proposed a method in Japanese Patent Application No. 59-201319 in which a coating layer for forming one of the groups of filter picture elements is formed using a coating solution containing a polyimide precursor solution and a coloring agent, the coating layer being then subjected to patterning by means of photolithography. FIG. 2 shows a flow chart of this method, and it will be appreciated that this method is considerably simplified in comparison with the method of FIG. 1.

According to the above method proposed by the present inventors, each group of filter picture elements can be formed relatively easily. However, each time each group of filter picture elements are to be formed,

an intermediate protective layer must be formed to protect the precedingly-formed group of picture element. The same procedure is also required for the conventional process of FIG. 1.

The formation of such an intermediate protective layer not only makes the production of the color filter complicated but also makes the overall thickness of the color filter greater. In addition, this adversely affects a flatness of a surface of the color filter, which affects display characteristics and thinness of a flat panel display such as a color LCD device.

In order to overcome the above problems, the present inventors have aimed at eliminating the intermediate protective layer and made extensive study and found the following.

When the second group of filter picture elements are formed without coating the first group of the filter picture elements with the protective layer, each filter picture element of the first group is damaged when the coating solution for forming the second group of filter picture elements is applied, but is hardly damaged at the time of etching for forming the pattern. The word "damage" here means that the first or preceding group of filter picture elements are subjected to cracks and wrinkles, and that the coloring material in the filter picture element dissolves therefrom, and that the filter picture element itself dissolves. It is thought that such phenomena are caused a solvent contained in the coating solution for forming the second group of filter picture elements.

DISCLOSURE OF THE INVENTION

It is an object of this invention to provide a color filter which eliminates the use of the above-mentioned intermediate protective layer, and enables a flatness of a surface of the color filter, and can make the overall thickness of the color filter smaller.

Another object of this invention is to provide a method of producing a color filter in which the above-mentioned intermediate protective layer can be omitted by imparting solvent-resistance, that is, a resistance to a solvent which solves a polyimide precursor solution, to the precedingly-formed group of filter picture elements.

A further object of this invention is to provide a technique of producing a color filter in which a dye which is soluble in the polyimide precursor solution is used as a coloring agent for coloring the polyimide, so that the coating solution has a uniform tinting and excellent coating properties.

The color filter according to the present invention of which cross-section is shown in FIG. 3 comprises a substrate 10 such as a light-transmitting glass plate, and a color filter layer 12 formed on one surface of the substrate 10. The color filter layer 12 comprises, for example, three groups of filter picture elements 14R, 14G and 14B having respective spectral characteristics corresponding respectively to red, green and blue. Each group has a number of filter picture elements R, G and B. The size of each filter picture element varies depending on the size of a light-receiving surface. For example, in a color liquid crystal television of a small size, the filter picture element has a square shape of a mosaic pattern one of longitudinal and transverse sides of which has several tens to several hundreds μm . Thus, the picture elements are arranged on the one surface of the substrate 10 in a matrix manner, and the arrangement is usually such that each adjacent filter picture elements have different colors, that is, different spectral

characteristics. As cross-sectionally shown in FIG. 4 and as in FIG. 3, light-intercepting layers 16 for intercepting light may be disposed at boundaries between adjacent filter picture elements R, G and B of the three groups 14R, 14G and 14B. The light-intercepting layers assumes a grid-like shape.

The filter picture elements R, G, B of each of the groups 14R, 14G and 14B are arranged on the one surface of the substrate in direct contact therewith. The thickness of the layer of each filter picture element R, G, B varies depending on the color strength to be desired. For example, it is approximately 0.5 to 2.0 μm . and preferably it is approximately 0.75 to 1.5 μm . Therefore, the difference in the layer thickness between the different filter picture elements is almost negligible, and the surface of the color filter 12 according to the present invention is flat and the color filter is thin as a whole. Other than an ordinarily-used glass plate, other light-transmitting material, such as a plastics plate, a flexible plastics film and a semi-conductor board incorporating electric elements, is used as the substrate 10. In a color LCD device, a transparent electrode layer constituting one of a common electrode and a picture element electrode is formed on one side of the color filter. In the case where the transparent electrode layer is formed on the underside of the color filter, the transparent electrode layer is, of course, pre-formed on the one surface of the substrate 10.

Each of the filter picture elements R, G and B comprises polyimide having excellent thermal resistance and light resistance, and a dye retained therein. It is preferred that the polyimide is excellent in transparency in order not to affect a light-transmitting ability required for the color filter. It is also preferred that the dye for effecting the coloring is excellent in thermal resistance and has an excellent solubility to the polyimide. Other than dye, the use of pigment for coloring the polyimide may be considered. However, in the case of pigment, the pigment is in the form of particles having a particle size, for example, of about 0.1 to 0.3 μm , and is liable to produce secondary particles, thereby increasing the particle size, so that it is difficult to disperse uniformly in the polyimide. In addition, the dispersed solids cause unevenness and stripes in the coating layer when the coating layer for the patterning of the filter picture elements is formed. On the other hand, the use of dye eliminates such problems. The polyimide can be easily patterned by means of photolithography which uses a photoresist as a mask. In this case, the polyimide is prepared as a polyimide precursor solution. The polyimide precursor solution comprises a solvent of a high polarity such as N-methyl-2-pyrrolidone and polyamic acid as polyimide precursor. Commercially-available and easily-available polyimide precursor solution is, for example, a stock solution of high viscosity of about 1200 centipoise. This highly-viscous solution can be diluted using N, N-dimethyl acetamide, N, N-dimethyl formamide, N-methyl-2-pyrrolidone, cyclohexanone, carbital derivatives, or cellosolve derivatives. For example, it can be adjusted to a suitable viscosity of several tens to several hundreds centipoise suited for a rotary coating operation. The dye can be sufficiently dissolved in such a solvent, so that it can be dispersed in the polyimide precursor solution easily and uniformly. In addition, when forming the coating layer, the dye having a solubility will not cause the above problems encountered with the pigment. The dye for each group of filter picture elements can be one kind of dye or can

be made by mixing two or three kinds of dyes together, and it is preferred that the amount of the dye used is as much as possible to provide a high color strength. However, if the amount is unduly excessive, there is encountered the disadvantage that the dye escape into the photoresist at a later step, a release agent for releasing the photoresist, and the subsequent upper coating layer. Therefore, preferably, the amount should be increased to such an extent that the dye will not escape. It is appropriate that the amount of dye used is equal to that of the polyimide in terms of weight %.

In the present invention, the temperature of the heat treatment for the precedingly-patterned filter picture elements, that is, the temperature of the post-baking is as high as possible so long as the thermal resistance of the dye is maintained, thereby promoting the conversion of the polyamic acid into the polyimide.

The conversion of the polyamic acid into the polyimide proceeds when the polyamic acid is dehydrated and is subjected to ring closure. The degree of proceeding becomes higher as the temperature of the heat treatment becomes higher. As to the polyimide of the heat-dehydration type, if the conversion is not carried out at a heat treatment temperature of about 400°C., the conversion is not complete. However, since the coating layer for forming the filter picture elements is formed by adding the coloring dye to the polyimide precursor solution, the upper limit of the temperature of the post-baking is limited by the thermal resistance of the dye. Therefore, it is preferred that dye of the type which can be well mixed in the polyimide precursor solution and has a high thermal resistance is used as the coloring dye. Suitable examples of such dyes are shown in Table 1 below. In Table 1, the thermal resistance of 250°C. means that when the heat treatment is carried out at 250°C. for a long time, the dye is somewhat subjected to fading but is practically usable. And, the thermal resistance of not less than 250°C. means that when the heat treatment is carried out at 250°C. for a long time, the dye is not subjected to any deterioration such as fading.

TABLE 1

Color	Kind	(coloring dyes)	
		Color index name	thermal resistance
Yellow	Azo dye	Solvent Yellow 19	250°C.
		Solvent Yellow 21	not less than 250°C.
		Solvent Yellow 77	250°C.
		Solvent Yellow 83	not less than 250°C.
Red	Azo dye	Solvent Red 122	not less than 250°C.
	Antraquinone dye	—	not less than 250°C.
Blue	Antraquinone dye	Acid Blue 129	250°C.
	Azine dye	Solvent Blue 49	250°C.
	Phthalocyanine dye	Solvent Blue 25	not less than 250°C.
	Triphenyl-methane dye	Acid Blue 9	not less than 250°C.
Black	Azo dye	Acid Black 155	not less than 250°C.

With respect to those dyes having a relatively low thermal resistance, it is preferred that a resin-surface modifier is added to the coating solution so as to impart water repellency and oil repellency to the surface of the coating layer. The resin-surface modifier imparts solvent resistant to the groups of filter picture elements and a block polymer having a functional segment having an excellent migration of resin like a perfluoroalkyl group and having water repellency and oil repellency.

A block polymer of vinyl monomers having, in addition to a functional segment, a compatible segment compatible with polyimide like an acrylic polymer is particularly preferred since the water and oil repellency is semi-permanent. Further, as the resin-surface modifier, a graft polymer of a functional comb shape which is synthesized by a copolymer of a macro monomer and a functional monomer and has an excellent interface-migrating property can be used. Further, as the resin-surface modifier, a mixture of a graft polymer of a functional comb shape and the above block polymer. The amount of the resin-surface modifier is usually 1 to 3%. If this amount is increased, the water and oil repellency is enhanced, but for example, if the amount is 5 to 10%, the uniformity of the coating layer for forming the groups of filter picture elements is lowered. Therefore, it is preferred that the amount is in such a range as not to lower the uniformity of the coating layer.

As is shown in a flow chart of the method of the present invention in FIG. 5, steps of forming intermediate protective layers for protecting the preexistingly formed groups of filter picture elements are totally omitted. When the light-intercepting layers and the groups of filter picture elements are all heat treated at high temperatures, so that the solvent resistance is sufficiently enhanced, a transparent protective layer covering the uppermost layer of the color filter, i.e., a top coat, can be omitted.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow chart of a process utilizing a conventional dyeing method:

FIG. 2 is a flow chart of the earlier-proposed process:

FIG. 3 is cross-sectional view of a color filter according to one embodiment of the present invention:

FIG. 4 is a cross-sectional view of a color filter according to another embodiment of the present invention; and

FIG. 5 is a flow chart of the process according to the present invention.

THE PREFERRED EMBODIMENT OF THE INVENTION

The three groups of filter picture elements 14R, 14G and 14B having the respective spectral characteristics corresponding respectively to red, blue and green as well as the grid-like light-intercepting layer 16 were formed on the one surface of the substrate 10 of a glass plate under the following conditions to form the color filter of FIG. 4 for use in a color LCD device. No damage of a nature mentioned above was found in the light-intercepting black layer 16, the group of blue filter picture elements 14B and the group of red filter picture elements 14R, and the color filter thus obtained was of a good quality although it had no intermediate protective layer. Compositions of the coating solutions and the formations of the groups of filter picture elements 14R, 14G and 14B are as follows:

COATING SOLUTIONS

(Light-intercepting layer 16)

Solvent black 3	1.0 g
Polyimide precursor solution (Semicofine manufactured by Toray Industries, Inc.)	5.0 g
Methyl cellosolve	15.0 g
Silane coupling agent	0.02 g
(Group of blue filter picture elements 14B)	
Acid blue 129	0.32 g

-continued

Polyimide precursor solution (Semicofine manufactured by Toray Industries, Inc.)	5.0 g
Methyl cellosolve	7.5 g
Silane coupling agent	0.02 g
(Group of red filter picture elements 14R)	
Acid red 257	0.5 g
Polyimide precursor solution (Semicofine manufactured by Toray Industries, Inc.)	5.0 g
Methyl cellosolve	8.5 g
Silane coupling agent	0.02 g
Resin-surface modifier	0.02 g
(Group of green filter picture elements 14G)	
Solvent yellow 77	0.5 g
Acid blue 7	0.5 g
Polyimide precursor solution (Semicofine manufactured by Toray Industries, Inc.)	5.0 g
Methyl cellosolve	8.5 g
Silane coupling agent	0.02 g

Each of the coating solutions, before being applied, was passed through a filter having a pore size of 0.5 μm to remove foreign matters.

(a) FORMATIONS OF PATTERNS

Each of the above coating solutions was applied by a spinner for 60 to 90 seconds, the spinner rotating at a speed of 1000 rpm. Then, the coating layer was left at room temperatures for 30 minutes for leveling purposes.

(b) FIRST PRE-BAKING

The substrate 10 was placed on a hot plate heated to 120° to 170° C. and dried for 3 to 15 minutes.

(c) COATING OF PHOTORESIST AND EXPOSURE TO LIGHT

Positive-type photoresist was applied by a rotary coater and dried by a hot plate at a temperature of 125° C. for 3 minutes and then was exposed through a photomask to ultraviolet light emitted from an ultra-high pressure mercury vapor lamp. The energy of the exposure was 80 mJ/cm².

(d) DEVELOPMENT AND ETCHING

The development was carried out using a developer of aqueous sodium hydroxide of 0.1 to 0.3N, and the coating layer was subjected to etching.

(e) RELEASE OF PHOTORESIST

Those portions of the photoresist not exposed to the light were removed using cellosolve acetate.

(f) POST-BAKING

The heat treatment was carried out in the air at 250° C. for 30 to 60 minutes.

The above steps were carried out for each color to complete the above color filter.

INDUSTRIAL APPLICABILITY

As described above, the present invention is suited for the color filter for color display or color separation for use in a color LCD device, a color video camera and the like, and particularly is best suited for such a device having picture elements of a high density and such a device having a large light-receiving surface since the flatness of the color filter surface and the reduction of the thickness of the color filter are achieved.

What is claimed is:

1. A color filter adapted to be placed on a light-receiving surface comprising:
 - (a) a substrate having one surface parallel to the light-receiving surface; and
 - (b) a color filter layer formed on said one surface of said substrate;
2. Said color filter layer comprising not less than two groups of filter picture elements having different

spectral characteristics, each of groups being composed of a number of said filter picture elements, each of said filter picture elements of each group comprising a polyimide and coloring dye retained in said polyimide, and each filter picture element being disposed in direct contact with said one surface of said substrate, said color dye being of a relatively high solubility in the polyimide polymer which provides the filter element with excellent transparency, excellent coating properties and uniform tinting, said dye having thermal resistance of at least 250° C.

2. A color filter according to claim 1, in which said substrate is a light-transmitting plate.

3. A color filter according to claim 1, in which said substrate has a transparent electrode layer on said one surface thereof.

4. A color filter according to claim 1, in which each of said filter picture elements is a square shape, said filter picture elements being arranged in a matrix manner.

5. A color filter according to claim 4, in which each adjacent filter picture elements in both transverse and longitudinal directions have different spectral characteristics.

6. A color filter according to claim 1, in which there are provided three groups of filter picture elements having respective spectral characteristics corresponding respectively to red, green and blue.

7. A color filter according to claim 6, in which a light-intercepting layer is disposed at a boundary between each adjacent filter picture elements of said three groups.

8. A color filter according to claim 7, in which said light-intercepting layer comprises polyimide and black dye retained in said polyimide.

9. A color filter according to claim 7, in which said light-intercepting layer is disposed in direct contact with said one surface of the substrate.

10. A color filter according to claim 1, in which a transparent protective layer is applied to an upper surface of said color filter layer.

11. A color filter according to claim 2, in which said substrate has a transparent electrode layer on said one surface thereof.

12. A color filter according to claim 8, in which said light-intercepting layer is disposed in direct contact with said one surface of the substrate.

13. A color filter according to claim 7, in which a transparent protective layer is applied to an upper surface of said color filter layer.

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United States Patent [19]

Latham et al.

[11] Patent Number: 4,822,718

[45] Date of Patent: Apr. 18, 1989

[54] LIGHT ABSORBING COATING

[75] Inventors: William J. Latham; Terry L. Brewer; Jeffry Hummingake, all of Rolla, Mo.

[73] Assignee: Brewer Science, Inc., Rolla, Mo.

[21] Appl. No.: 825,855

[22] Filed: Feb. 4, 1986

[51] Int. Cl. 4 G03C 1/76

[52] U.S. Cl. 430/271; 430/521;
430/522; 430/512

[58] Field of Search 430/271, 521, 522, 512

[56] References Cited

U.S. PATENT DOCUMENTS

2,791,504	5/1957	Plambeck	430/271
2,892,716	6/1959	Martin	96/115
4,064,113	12/1977	D'Alelio	524/84 X
4,102,683	7/1978	DiPiazza	96/384
4,230,939	10/1980	de Bont et al.	430/945
4,242,437	12/1980	Rohloff	430/271
4,357,416	11/1982	Fan	430/302
4,362,809	12/1982	Chen et al.	430/312
4,370,906	1/1983	O'Toole et al.	430/312
4,376,162	3/1983	Kawata et al.	430/510

OTHER PUBLICATIONS

R. Rubner et al, "A Photopolymer-The Direct Way to Polyimide Patterns", Photographic Science and Engineering, vol. 23, No. 5, 1979, pp. 303-309.

P. Tschopp, "Use of UV-Absorbers", No. 22217, Research Disclosure, Oct. 1982; p. 327.

Fok, Society of Photographic Scientists and Engineers, Inc. Seminar, 1968, pp. 116-131.

Listran, Swanson, Walland and Campbell, SPIE Society of Photo-Optical Instrumentation Engineers Conf., Santa Clara, CA, Mar. 1984.

Hackh's Chemical Dictionary, Third Edition, 1944, pp. 132, 230.

Lin, Purdes, Saller and Hunter, International Electron Device Meeting, San Francisco, CA, Dec. 1982, p. 399.

Potter et al, Engineering Reports, No. 5, p. 1, May 1984.

R. D. Coyne and A. J. Brewer, Kodak Microelectronics Seminar, San Diego, CA, Nov. 1983.

Brewer, Carlson and Arnold, Journal of Applied Photographic Engineering, vol. 7, No. 6, Dec. 1981.

Ting and Liguw, SPIE Society of Photo-Optical In-

strumentation Engineers Conf., Santa Clara, CA, Mar. 1984.

O'Toole, Liu and Chang, IEEE Transactions on Electron Devices, Edition 2a, No. 11, Nov. 1981, pp. 1405-1410.

Chang, E. D. Liu, and M. M. O'Toole, 1981 Symposium on VLSI Technology, Digest of Technical Papers, Maui, HI, Sep. 1981.

A. O. Weiss, Semiconductor International, Apr. 1983, p. 82.

K. Harrison and C. Takemoto, Kodak Microelectronics Seminar, San Diego, CA, Nov. 1983.

Burggraaf, Semiconductor International, vol. 66, Feb. 1984.

Lin, Marriot, Orvek and Fuller, SPIE Society of Photo-Optical Instrumentation Engineers Conf., Santa Clara, CA, Mar. 1984.

Carlson and Arnold, Kodak '80 Interface, Oct. 1980, pp. 109-113.

Punyakumleard et al, ACS National Meeting, St. Louis, MO, Apr. 1984.

Y. C. Lin, Sue Jones, G. Fuller, IEEE, Los Angeles, CA, May 1983, Apr. 1984.

P. Burggraaf, Semiconductor International, Nov. 1983.

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Assistant Examiner—Cynthia Hamilton

Attorney, Agent, or Firm—Cohn, Powell & Hind

[57]

ABSTRACT

A broad spectrum light absorbing medium to be coated over photosensitive layers, such as a photoresist for integrated circuit "chips" to act as a true surface for autofocus of the camera used to expose the photoresist. The product may also be used where a light impermeable, high contrast or black coating is needed, such as, in liquid crystal displays and light emitting diodes, photodiodes, solid state lasers, or patterning apertures on light-wave modulators. The coating absorbs light from 200 to 1000 nanometers. The coating has a polymer vehicle which can form a tightly adhering, thin, smooth and uniform coating. The coating includes a light absorbing dye. This light absorbing layer may be imageable.

20 Claims, No Drawings

LIGHT ABSORBING COATING

This is a continuation-in-part of U.S. patent application Ser. No. 638,258 filed Aug. 6, 1984 and is a continuation-in-part of U.S. patent application Ser. No. 431,798 filed Sept. 30, 1982. Application Ser. No. 638,258 is a divisional application of application Ser. No. 431,709. The disclosures of these two applications are incorporated by reference herein.

BACKGROUND AND SUMMARY OF THE INVENTION

In recent years many electronic devices have been developed which emit or in some way modulate light. Because of these developments a need has arisen for a black coating which can be patterned by any of the several processes common in the microelectronics industry. This black coating may either be used to protect light sensitive areas of a device from light or to enhance contrast between light emitting or reflecting areas on a device and those areas which should appear darker. The polymer coating must do much more than merely absorb light. Black paint for example could not be used. The coating should be patternable preferably by a process already used in the industry. One process involves coating positive photoresist exposing it to light and developing the photoresist and an underlying layer in hydroxide solution. This basic process is called a wet process or a wet etch. Another process involves coating resist on a substrate patterning the resist, etching the substrate and then etching a sublayer under the substrate using a plasma or a reactive ion etch. This is called a dry etch in the art. Another requirement of the coating is that the polymer coating should have dielectric properties. As a part of an electrical device it should have a high dielectric strength and a high resistivity. A third requirement is that the coating should be uniform. It should adhere well to common substrates such as silicon oxide and aluminum. The coating should be a strong absorber of light at the wavelengths of interest and it should have high thermal stability and it should be durable. Also, the film thickness must be compatible with the thickness of the electrical device while still providing sufficient light attenuation.

In the art one material currently sold by Polytronics of Richardson, Tex. attempts to meet some of the above requirements but does not meet all of them. It contains a polymer solution filled with finely ground carbon. The polymer used is polyimide which imparts thermal stability but the material can be patterned only by a wet process, it cannot be dry etched. The material has extremely low resistivity and is thus not compatible with many electronic devices. Moreover the film is not uniform due to the carbon particles and light absorption per unit of film thickness is very low. The art has attempted to solve the problem of protecting light sensitive areas of a device in other ways including by depositing an insulating layer on the device and patterning a metal on top of the insulating layer. The metal shields portions of the device from light. However, this process is very time consuming and more expensive than using an opaque organic film. In addition many users do not like this system since they do not wish to reflect light because of affects on peripheral light sensitive devices or because the appearance of a very shiny surface is not satisfactory in their device. A further way of enhancing contrast in the art has been to deposit an anti-reflection

layer such as an indium-tin-oxide on a part of the device which should appear optically darker. These layers are very limited in that they work only over a relatively narrow band of wavelengths and they require a more complex and longer process and are difficult to rework.

One final approach which the art has used has been to use a filter which is overlaid on the device that is, the filter is not deposited directly on the device. Due to the size and geometry of the filter and the complexity of the filter patterns these devices are limited due to problem of aligning the filter precisely with the underlying device.

Applicants' invention solves the problems of the prior art by using preferably a polymer precursor and soluble dyes which form the uniform containing this film with extremely good insulating properties, good adhesion properties, wet and dry development characteristics with a photoresist system and a very high light absorbance in a desired wavelength range from ultraviolet through the visible and through the infrared spectrum. Applicants' coating material has a film thickness compatible with electronic and electrical devices and has a very high resolution of features compatible with such electrical and electronic devices. The light absorbing film demonstrates extremely good thermal, chemical and aging stability and may remain an integral part of an electrical or electronic device.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Applicants' coating material has a very broad application. For example, it may be used to replace state of the art mask inspection systems in microelectronic photolithographic processes. Mask inspection systems allow process engineers to inspect for mask defects without taking a printer off line. Typically a glass wafer with a thin layer of chromium and a layer of photoresist are exposed in a printer. The resist is developed to provide an etch mask for the chromium and the chromium is subsequently etched. The chrome pattern on the glass wafer is compared in a mask inspection system to the original mask pattern. Inspection systems typically employ a relatively narrow band of wavelengths 450-650 nanometers for KLA instruments and 510 or 525 nanometers for Nipon Jido Seigo instruments. Applicants' coating absorbs light at these wavelengths and furnishes sufficiently high contrast for the inspection system to operate. The coating system is patterned using a positive photoresist and developer and eliminates the need for a chrome plating and etch. It thus shortens the process time for mask inspection and allows inspection to be done without additional process equipment and without using chromium which is an environmental pollutant.

Applicants' coating can also be used to improve the performance of projection printer automatic focus systems by coating a light absorbing film on photoresist and thereby reducing the intensities of all reflected rays except that from the top surface itself. Focus is an important factor in semi-conductor and other microelectronic manufacture. Automatic focus mechanisms of projection printers typically employ a light source and a detector which senses reflected light. When light strikes the surface of the film some light is reflected and some passes through the film and is reflected at the interface of succeeding layers. These multiple reflections can cause an automatic focus mechanism to function improperly. Applicants' coating absorbs the near

infrared light emitted by the laser diodes and light emitting diodes typically used in focusing systems. It thus reduces the intensity of light reflected from all but the top surface of a multi-layer system improving the performance of automatic focus systems. Typically applicants' coating would be spin cast on top of a photoresist. When used in an automatic focusing system applicants' coating would not include the dyes which absorb the light in the blue and near ultra-violet wave lengths typically used to expose the photoresist. The coating vehicle may be water soluble or may be solvent soluble and it is stripped when the photoresist is developed. It therefore has negligible effect on the photoresist performance. The coating is applied in such a thin layer that the thickness of the coating plus the photoresist does not exceed the depth of focus limit of the optical machinery. Typically the coating would be spin cast on top of a prebaked photoresist. The coating need not be baked but may be baked if desired for example in a convection oven at 90° C. for a half hour to evaporate the solvent. The coating would be left intact during the focus and exposure steps in a projection printer and the coating would be immediately stripped when the exposed photoresist is immersed in or sprayed with an aqueous developer. In all other respects the automatic focusing process and equipment are conventional.

Applicants' material includes a polymer or a polymer precursor and soluble dyes that are effective to form a uniform, thin, tightly bonded continuous film with good insulating properties, good adhesion properties, wet and/or dry development properties with photoresist systems and which has high light absorbance in the desired wavelength range from ultraviolet through the visible and into through the infrared spectrum. The film thickness is compatible with electrical and electronic devices and the coating has high resolution required by electrical and electronic devices such as microelectronic devices. The light absorbing film also demonstrates good thermal, chemical and aging stability to remain an integral part of an electrical system. The coating material is a solution containing polyimide or polyimide precursor and required solvent soluble dyes. Because the material is not carbon or pigment filled it has very high resistivity and very high dielectric strength and does not interfere with performance of electrical or electronic devices on which it is coated. The material can be patterned by both a wet process and a dry etch. Typically the product is highly absorbing in the near ultraviolet and visible and even into the near infrared spectrum through 1000 nanometers. The material has no large particles since it is a solution and coatings are very uniform. Applicants' material adheres very well to silicon, silicon oxide and aluminum substrates. The material has extremely high thermal stability and is highly durable. Applicants' product may be used and applied in a conventional manner. For example, the material may be spun or sprayed on any conventional electrical or microelectronic substrate. For example, spinning at 4000 rpm's will typically give a film which is 5 microns thick. The material may be baked to remove solvent and to crosslink the polymer precursor. If the product is to be wet etched a positive photoresist may be spun on top. The resist is baked, exposed and developed as is conventional in the art. Applicants' light absorbing layer may develop out where the photoresist is removed and so may be patterned at the same time as the photoresist. If the material is to be dry etched a layer of aluminum or other suitable etch mask may be

deposited on top of the light absorbing layer and patterned. The substrate is then placed in a chamber for a reactive ion or plasma etching and the light absorbing layer is etched out in areas not covered by the etch mask. After patterning the light absorbing layer may be baked at a higher temperature to harden the polymer.

Depending upon the method and the application the light absorbing layer may be a few microns to a few tenths of microns in thickness. Spinning typically yields films from one micron to ten microns in thickness. Conventional spraying may result in thicker films which may be as thick as twenty-five microns. Applicants' product absorbs strongly in the near ultraviolet, the visible spectrum and the visible spectrum from 200 to 750 nanometers and depending on the dye formulation may absorb strongly from 200 to 1000 nanometers. For example a five micron film of applicants' product may transmit less than one percent of all light from 200 to 750 nanometers or from 200 to about 1000 nanometers. Applicants' product is unique in that very small geometries can be patterned in it. Wet processing of a five micron thick film for example can resolve lines as small as five microns. Dry etching processing can resolve even smaller lines.

The resistivity of its light absorbing layer is 3×10^{15} ohm-cm or more and the dielectric strength exceeds 7×10^5 volts per centimeters. These are outstanding electrical characteristics for an organic film and far better than can be expected with a polymer film filled with carbon or other pigments or any conventional material.

Some specific applications for applicants' light absorbing coating include protecting light sensitive circuitry and enhancement of contrast in liquid crystal displays, electro-luminescent displays, plasma displays and imaging systems such as charge-coupled devices for telecommunications and video cameras. Applicants' light absorbing coating may also protect light sensitive areas of light-emitting diodes, avalanche photodiodes, and solid state lasers. Applicants' product may be used to pattern apertures on light-wave modulators and other similar equipment.

The vehicle for applicants' light absorbing layer will typically include a polyimide precursor which reacts in use to form a polyimide resin. The precursor typically includes a polyamic acid prepared by reacting oxydianiline (ODA) with pyromellitic dianhydride (PMDA) or may be prepared by reacting ODA with PMDA and benzophenone tetracarboxylic dianhydride (BTDA). Other equivalent polyamic acids and polyamic precursors may be used. The reactants for the polyimide precursors are typically included in approximately stoichiometric amounts. Some formulations may include water soluble polymers such as polyvinyl/pyrrolidone and/or other conventional resins such as novalac. The dyes may be chosen from soluble organic dyes which are effective to absorb over a broad spectrum of light or from effective combinations of dyes. Exemplary dyes are as follows curcumin, Solvent Blue 45 (Saviniyl Blue RLS Sandox Chemical Corporation), Solvent Red 92 (Saviniyl Scarlet RLS Sandox Chemical Corporation), Solvent Blue 44 (Saviniyl Blue GLS Sandox Chemical Corporation), Solvent Blue 35 (Hytherm Blue B-200% Morton Chemical), Solvent Red 111 (Morton Red AAP Morton Chemical Company), Solvent Orange 11 (Orasol Orange G Ciba-Geigy Corporation), Pylakrome Green (Pylam Products), IR-99 (American Cyanamid), IR-125 (Exciton Chemical Company) and Solvent Red

127 (TM, Sandoz Chemical Corporation). The dyes and vehicle or vehicle precursor are included with a solvent system having a low surface energy solvent so that the entire system is cosoluble. A typical solvent would include cyclohexanone.

The invention will be further understood by reference to applicants' examples included herein.

EXAMPLE 1

Using the following coating formulation:

58.5% polyimide precursor (ODA and PMDA)	10
7.3% N-methyl pyrrolidinone	
21.9% cyclohexanone	
4.4% Solvent Blue 45	
3.4% Solvent Red 92	15
3.9% Solvent Blue 44	
0.5% curcumin	

a black coating was prepared by stirring the mix for several hours. The mix was then filtered to remove undissolved material. The coating may be used as a 20 black background contrast coating to enhance the contrast of light emitting diode and liquid crystal displays. The coating may also be used as a background coating to eliminate scatter and reflected light in detectors such as photoelectric cells and photo diodes. The coating 25 may be coated by conventional spin or spray techniques on a substrate, baked to cure at 90° C. for 30 minutes, and at 90°-130° C. for 30 minutes, coated with photore sist, cured, exposed and developed by conventional processes. The coating may have a subsequent cure at 30 200° C. for 30 minutes. The coating absorbs substantially all light between 200-750 nm.

EXAMPLE 2

Using the following coating formulation:

58.5% polyimide precursor (ODA and PMDA)	35
7.3% N-methyl pyrrolidinone	
21.0% cyclohexanone	
4.0% Solvent Blue 45	
3.4% Solvent Red 92	40
4.3% Pylakrome Green	
0.5% curcumin	

a black coating was prepared, as described for Example 1.

EXAMPLE 3

Using the following coating formulation:

58.5% polyimide precursor (ODA, and PMDA)	45
7.3% N-methyl pyrrolidone	
21.9% cyclohexanone	
4.4% Solvent Blue 35	50
3.4% Solvent Red 92	
3.9% Solvent Blue 44	
0.5% curcumin	

a black coating was prepared, as described for Example 5 7.

EXAMPLE 4

Using the following coating formulation:

57.5% polyimide precursor (ODA and PMDA)	60
7.3% N-methyl pyrrolidone	
21.9% cyclohexanone	
4.4% Solvent Blue 45	
3.4% Solvent Red 111	65
3.9% Solvent Blue 44	
1.5% Solvent Orange 11	

a black coating was prepared, as described for Example 1.

EXAMPLE 5

Using the following coating formulation:

58.5% polyimide precursor (ODA, BTDA, and PMDA)	
7.3% N-methyl pyrrolidone	
21.9% cyclohexanone	
4.4% Solvent Blue 45	
3.4% Solvent Red 92	
3.9% Solvent Blue 44	
0.5% curcumin	

a black coating was prepared, as described for Example 1.

EXAMPLE 6

Using the following coating formulation:

43.9% polyimide precursor (ODA and PMDA)	
11.7% N-methyl pyrrolidone	
35.2% cyclohexanone	
3.3% Solvent Blue 45	
2.6% Solvent Red 92	
2.9% Solvent Blue 44	
0.4% curcumin	

a black coating was prepared, as described for Example 1.

EXAMPLE 7

Using the following coating formulation:

57.5% polyimide precursor (ODA and PMDA)	
7.3% N-methyl pyrrolidinone	
21.9% cyclohexanone	
4.4% Solvent Blue 45	
3.4% Solvent Red 92	
3.9% Solvent Blue 44	
0.5% curcumin	
1.0% IR-99	

a black coating was prepared, as described for Example 1. The coating absorbs substantially all light between 200 and 1000 nm. This coating is especially useful as a 40 background and contrast coating for light emitting diodes and sensors which operate in the near infrared range.

EXAMPLE 8

Using the following coating formulation:

43.9% polyimide precursor (ODA and PMDA)	
7.3% N-methyl pyrrolidone	
21.9% cyclohexanone	
4.4% Solvent Blue 45	
3.4% Solvent Red 92	
3.9% Solvent Blue 44	
0.5% curcumin	
1.0% IR-125	

a black coating was prepared, as described for Example 7.

EXAMPLE 9

Using the following coating formulation:

56.5% polyimide precursor (ODA and PMDA)	
7.3% N-methyl pyrrolidone	
21.9% cyclohexanone	
4.4% Solvent Blue 35	
3.4% Solvent Red 111	
3.9% Solvent Blue 44	
1.5% Solvent Orange 11	
1.0% IR-125	

a black coating was prepared, as described for Example 7.

EXAMPLE 10

Using the following coating formulation:

43.1% polyimide precursor (ODA and PMDA)
 11.7% N-methyl pyrrolidone
 35.2% cyclohexanone
 3.3% Solvent Blue 45
 2.6% Solvent Red 92
 2.9% Solvent Blue 44
 0.4% curcumin
 0.8% IR-125

a black coating was prepared, as described for Example 7.

EXAMPLE 11

Using the following coating formulation:

57.5% polyimide precursor (ODA, PMDA, BTDA)
 7.3 N-methyl pyrrolidone
 21.9% cyclohexanone
 4.4% Solvent Blue 45
 3.4% Solvent Red 92
 3.9% Solvent Blue 44
 0.5% curcumin
 1.0% IR-125

a black coating was prepared, as described for Example 7.

EXAMPLE 12

Using the following coating formulation:

225 g Polymide precursor (ODA and PMDA)
 27 g Novolac
 211 ml N-methyl-pyrrolidinone
 692 ml Cyclohexanone
 56 g Solvent Red 127
 56 g Solvent Red 92

a mask inspection coating was prepared by stirring the mix for several hours. The mix was then filtered to 0.45 microns to remove undissolved material. The coating may be applied by spinning or other techniques. For example, it may be spin coated to a thickness of 0.3 micron on a glass wafer and used in place of a chromium layer in a mask inspection system. A 0.3 micron film of the coating absorbs at least about 90% of the light used by mask inspection systems, about 500-600 nm.

EXAMPLE 13

Using the following coating formulation:

4.8 g 15K polyvinyl pyrrolidone
 95.2 g H₂O
 1.0 g IR-125 anhydro-1,1-dimethyl-2-[7[1,1-dimethyl-3-(4-sulfobutyl)-2-(1H)-benz(e)indolinylidene]-1, 3,5-heptatrienyl]-4-sulfobutyl-1H-benz(e)indolium hydroxide sodium salt.

an automatic focus coating was prepared by stirring the PVP in room temperature water until dissolved, about one hour. The IR-125 is added to the solution and stirred for about three hours. The solution is then filtered to remove undissolved dye and polymer. The coating may be applied by spin coating to a film thickness of 700 angstroms. The coating absorbs the light in the 650-1000 nanometer range used by automatic focus mechanisms.

It will be appreciated by those skilled in the art that variations in the invention disclosed herein may be made without departing from the spirit of the invention. The invention is not to be limited by the specific em-

bodiments disclosed herein but only by the scope of the claims appended hereto.

We claim:

1. A broad spectrum light absorbing coating material for microelectronic photolithography consisting essentially of a polyimide precursor vehicle and at least one soluble light absorbing dye in a solvent system, the dye being substantially completely soluble in the solvent and vehicle system and being effective to absorb substantially all light across a broad spectrum of light, from in the ultra violet spectrum to in the infra red spectrum, when the coating is coated on a microelectronic photolithographic substrate, the coating system having a high electrical resistivity and a high dielectric strength when coated on a substrate, and being effective to provide a uniform, tightly adhering coating, the coating being photolithographically imagable and effective to produce microelectronic images having fine line resolution and being developable and etchable by wet and dry etch microelectronic photolithography processes, the coating having a high specific absorptivity over a broad spectrum of light effective to provide a substantially black coating.
2. The light absorbing coating material of claim 1 wherein the vehicle is selected from the group consisting of polyamic acids.
3. The light absorbing coating of claim 2 wherein the vehicle is selected from the group consisting of oxydianiline and pyromellitic dianhydride or oxydianiline, pyromellitic dianhydride and benzophenone tetracarboxylic dianhydride, the vehicle components being present in approximate stoichiometric amounts.
4. The light absorbing coating material of claim 1 wherein the coating material is effective to absorb substantially all light in the range of about 200 to 750 nanometers, when coated on a substrate.
5. The light absorbing coating material of claim 1 wherein the coating material is effective to form a high contrast coating and wherein the dye is selected from the group consisting of curcumin, Solvent Blue 45, Solvent Red 92, Solvent Blue 44, Solvent Blue 35, Solvent Red 111, Solvent Orange 11, Pylakrome Green, IR-99, anhydro-1, 1-dimethyl-2-[7[1,1-dimethyl-3-(4-sulfobutyl)-2-(1H)-benz(e)indolinylidene]-1,3,5-heptatrienyl]-4-sulfobutyl-1H-benz(e)indolium hydroxide sodium salt and Solvent Red 127 and mixtures thereof.
6. The light absorbing coating material of claim 1 wherein the coating has an electrical volume resistivity of at least about 3×10^{15} ohm-cm, when coated on a substrate.
7. The light absorbing coating material of claim 1 wherein the coating has a dielectric strength of at least about 7×10^5 V/cm, when coated on a substrate.
8. A light absorbing coating material for improving the performance of automatic focus equipment used in microelectronic photolithography consisting essentially of at least one soluble light absorbing dye in a vehicle and solvent system, the dye being effective to absorb substantially all unreflected light, from about 200 to about 1000 nanometers across the spectrum used in automatic focus processes, when coated on a microelectronic substrate, and being effective to provide a thin, uniform coating, the coating being compatible with subsequent processing of the microelectronic substrate including being readily removable by subsequent processing of the microelectronic substrate.

9. A light absorbing coating material for mask inspection systems used in microelectronic photolithography consisting essentially of at least one soluble light absorbing dye in a vehicle and solvent system, the dye being effective to absorb substantially all light across the spectrum used in microelectronic photolithography mask inspection systems, from about 200 to about 1000 nanometers, and being photolithographically imagable and developable in the mask inspection process, the coating being effective to provide a thin, uniform, coating and being effective to produce images having fine line resolution when used in a microelectronic photolithographic mask inspection system.

10. The automatic focus equipment light absorbing material of claim 8 wherein the vehicle is selected from the group consisting of polyimide precursors.

11. The light absorbing coating of claim 8 wherein the vehicle is selected from the group consisting of oxydianiline and pyromellitic dianhydride or oxydianiline, pyromellitic dianhydride and benzophenone tetracarboxylic dianhydride, the vehicle components being present in approximate stoichiometric amounts.

12. The light absorbing coating of claim 8 wherein the coating material is effective to absorb substantially all light in the range of about 650 to 1000 nanometers.

13. The automatic focus light absorbing coating of claim 8 wherein the dye is anhydro-1,1-dimethyl-2-[7[1,1-dimethyl-3-(4-sufobutyl)-2-(1H)-benz(e)indolinylidene]-1,3,5-heptatrienyl]-4-sulfobutyl)-1H-benz(e)indolium hydroxide sodium salt.

14. The light absorbing coating of claim 8 wherein the coating has an electrical volume resistivity of at least about 3×10^{15} ohm-cm and a dielectric strength of at least about 7×10^5 v/cm, when coated on a substrate.

15. The mask inspection light absorbing material of claim 9 wherein the vehicle is selected from the group consisting of polyimide precursors.

16. The light absorbing coating of claim 15 wherein the vehicle is selected from the group consisting of oxydianiline and pyromellitic dianhydride or oxydianiline, pyromellitic dianhydride and benzophenone tetracarboxylic dianhydride, the vehicle components being present in approximate stoichiometric amounts.

17. The light absorbing coating of claim 9 wherein the coating material is effective to absorb substantially all light in the range of about 500 to 600 nanometers.

18. The light absorbing coating of claim 9 wherein the dye is selected from the group consisting of solvent red 127, solvent red 92 and mixtures thereof.

19. The light absorbing coating of claim 9 wherein the coating has an electrical volume resistivity of at least about 3×10^{15} ohm-cm and a dielectric strength of at least about 7×10^5 v/cm, when coated on a substrate.

20. A broad spectrum light absorbing coating material for microelectronic photolithography consisting essentially of a polyimide precursor vehicle and at least one soluble light absorbing dye in a solvent system, the dye being substantially completely soluble in the solvent and vehicle system and being effective to absorb substantially all light across a broad spectrum of light, from about 200 nanometers to about 1000 nanometers, when the coating is coated on a microelectronic photolithographic substrate, the coating system having a high electrical resistivity and a high dielectric strength when coated on a substrate, and being effective to provide a uniform, tightly adhering coating, the coating being photolithographically imagable and effective to produce microelectronic images having fine line resolution and being developable and etchable by wet and dry etch microelectronic photolithography processes, the coating having a high specific absorptivity over a broad spectrum of light effective to provide a substantially black coating.

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United States Patent [19]

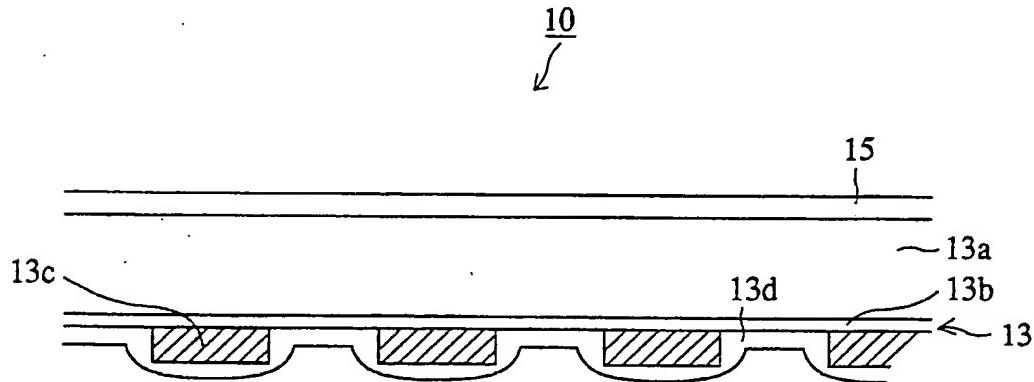
Sato et al.

[11] Patent Number: 5,527,649
[45] Date of Patent: Jun. 18, 1996**[54] METHOD FOR FORMING A SUBSTRATE HAVING A LIGHT SHIELDING LAYER**5,142,391 8/1992 Fujiwara et al. 359/67
5,186,801 2/1993 Matsumura et al. 204/181.1
5,372,902 12/1994 Yamashita et al. 430/7**[75] Inventors:** Haruyoshi Sato, Kawasaki; Toru Nakamura, Yokohama; Hitoshi Yuasa, Yokohama; Yutaka Otsuki, Yokohama; Hiroyoshi Omika, Yokohama; Norikatsu Ono, Narashino; Tadafumi Shindo, Tokyo, all of Japan*Primary Examiner*—Charles L. Bowers, Jr.
Assistant Examiner—John A. McPherson
Attorney, Agent, or Firm—Darby & Darby**[73] Assignees:** Nippon Oil Co., Ltd.; Dai Nippon Printing Co., Ltd., both of Tokyo, Japan**[21] Appl. No.:** 249,754**[22] Filed:** May 26, 1994**[30] Foreign Application Priority Data**May 28, 1993 [JP] Japan 5-127588
May 9, 1994 [JP] Japan 6-095275**[51] Int. Cl. 6** G02F 1/1335**[52] U.S. Cl.** 430/7; 430/20; 430/321**[58] Field of Search** 430/321, 5, 7,
430/20**[57]****ABSTRACT**

A method for preparing a substrate having a light-shielding layer involves forming a photosensitive coating film on a transparent electrically conductive layer formed on a transparent substrate, exposing the photosensitive coating film via a mask exhibiting light transmitting properties, removing and developing the coating film for exposing the transparent electrically conductive layer and electrodepositing a dark-hued coating on the exposed transparent electrically conductive layer for forming the light-shielding layer, and heating the light-shielding layer. The substrate having the light-shielding layer has a volume resistivity of 1×10^2 ohm-cm or higher and may be used for a counterelectrode substrate for a TFT array substrate incorporated in a liquid crystal display device.

[56] References Cited**U.S. PATENT DOCUMENTS**

4,902,592 2/1990 Matsumura et al. 430/7

14 Claims, 1 Drawing Sheet

11—

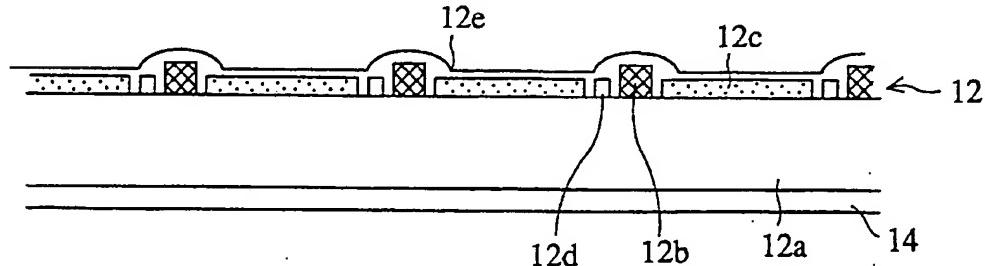
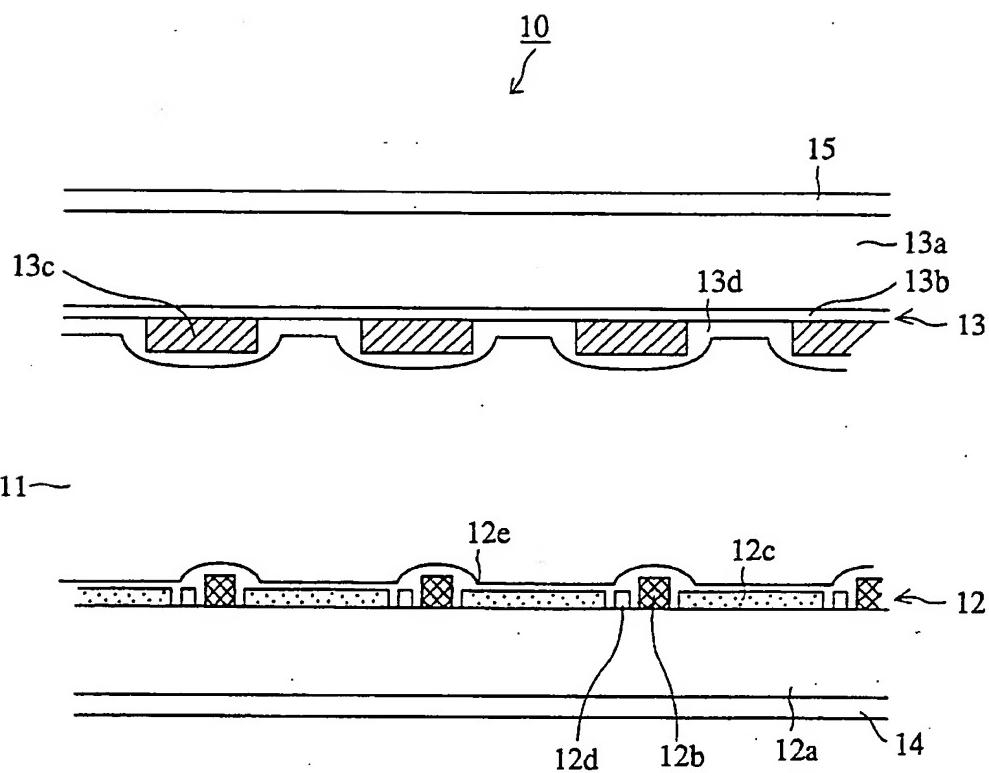


FIG. 1



**METHOD FOR FORMING A SUBSTRATE
HAVING A LIGHT SHIELDING LAYER**

BACKGROUND OF THE INVENTION

This invention relates to a method for forming a substrate having high definition and high light-shielding capability. More particularly, it relates to a method for forming a substrate which has a light-shielding layer and which may be utilized for preparing a color filter employed in particular for a liquid crystal display device, and to a substrate having the light-shielding layer.

This invention also relates to a counterelectrode substrate for a thin film transistor (referred to as TFT) array substrate for black and white display which is superior in high definition and light-shielding capability and which may be prepared by a simple process, and to a liquid crystal display device for black and white display (LCD).

As a typical example of the color liquid crystal display device, there has hitherto been known a TFT (thin film transistor)—active matrix color liquid crystal device. The device includes a substrate arranged on an inner polarizing plate, a thin film transistor (TFT) and a pixel electrode driven by the TFT arranged on the substrate, and an inner alignment layer contacted with both the TFT and the pixel electrode. On its outer side, the device includes a liquid crystal layer having an outer alignment layer and an outer polarizing plate arranged on the outermost side. Between the outer alignment layer and the outer polarizing plate, there is mounted a color filter having a black light-shielding layer (black matrix) and colored layers, such as red-hued layer, green-hued layer and blue-hued layer on a transparent electrically conductive layer formed on the transparent substrate. For producing the color filter, there are currently proposed a dyeing method, a dye-pigment dispersion method, a printing method, an electrodeposition method and a transfer method. With any of these known methods, the precision in the arraying of the respective colored layers, such as red-hued, green-hued and blue-hued layers, herein occasionally abbreviated to R, G, B and BL layers, respectively, is of utmost importance. Above all, the black-hued layer, that is the light-shielding layer, needs to be positioned not only in registry with the counterelectrode substrate to avoid light leakage in the vicinity of the pixel electrode but also without voids between the other colored layers and the light-shielding layer significantly influences the picture quality such as contrast. Consequently, the current practice is to produce the light-shielding layer with high precision and to form other colored layers so as to be overlapped to some extent with the light-shielding layer. For example, an evaporated film of metal such as chromium is patterned using a photolithographic technique to produce a black matrix and the color layers of R, G and B layers are formed with small amounts of overlap with the black matrix at the boundary regions thereof.

With the thin film transistor (TFT) display device for black and white display, which has a construction similar to the above-mentioned color liquid crystal display device, a transparent substrate formed with a light-shielding layer (black matrix) is provided in place of the R, G, and B layers of a color filter, and functions as a counterelectrode substrate. In preparing the counterelectrode substrate, a resist is coated on a metal chromium layer formed by sputtering on a glass substrate, and a black matrix is formed by light exposure, development, etching and film exfoliation. A transparent ITO film is subsequently formed by sputtering on the entire surface.

However, if a light-shielding layer is formed of metal, manufacture-related problems are presented in that the evaporation method or lithography is susceptible to pinholes and involves a complicated process, and that the light-shielding film formed of metal has high light reflectance and leads to inferior viewing properties of the display device. Above all, with the TFT black and white display device, the vacuum process needs to be carried out twice in order to produce the black matrix and the electrode. If the method of overlapping the boundary regions of the colored layers is employed for the preparation of the color filter, it is not possible to produce a color filter having superior surface planarity which is strongly desired when the color filter is used for the color liquid crystal display device.

In order to overcome these problems, a method of employing a photosensitive resin composition admixed with pigments of black or the like dark or thick colors has been proposed in the Japanese Laid-Open Patent Publications Nos. 63-314501, 1-293306 and 5-34514. Specifically, a method of forming a photosensitive resin composition previously colored in a dark color on a transparent substrate, exposing via a pattern mask only the portions of the resin composition required as a light-shielding layer, for curing the resin composition and developing and removing only the unexposed portions of the resin composition, a method of forming a layer of a photosensitive resin composition previously colored to have a thick color on a substrate on which R, G and B layers have been formed, exposing the reverse substrate surface, that is the substrate surface not having the layer of the photosensitive resin composition, to light for curing the photosensitive resin composition and developing and removing only the unexposed portion, and a combination of these methods, are disclosed. However, the photosensitive resin composition colored to have a dark color hue exhibits high light absorption so that curing cannot proceed to a sufficient depth on exposure to light. Consequently, the photosensitive resin composition colored to have a thick hue tends to be removed during removal by development so that the light-shielding layer having a high light-shielding capability can hardly be produced. In addition, the photosensitive resin composition having its exposed portion cured by photopolymerization is frequently employed. In light exposure in atmospheric air, curing is obstructed significantly by oxygen contained in atmospheric air, such that complex preventative measures such as provision of an oxygen interrupting film or employing an atmosphere free of oxygen, such as vacuum or an argon atmosphere, are needed in carrying out the light exposure. Although it may be envisaged to eliminate such cumbersome operations by increasing the amount of light exposure to an extreme degree, reflection, scattering or leakage of light is increased, while the substrate temperature tends to be raised, thus presenting difficulties in the formation of the high-precision light-shielding layer.

On the other hand, if the photosensitive resin composition containing black-hued or nearly black-hued pigment is employed as a black matrix for a counterelectrode substrate for a TFT array substrate, and a transparent substrate having a transparent electrode is employed as a counterelectrode substrate, it is necessary to provide a transparent electrode by sputtering on the overall surface, because the black matrix itself lacks electrical conductivity. The reason is that, if the liquid crystal on the black matrix is not responsive to electrical voltage, the liquid crystal portion in the vicinity of pixels undergoes light leakage during voltage-on time with the normally white system employed in the TFT array system, thus lowering the contrast.

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SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for forming a substrate having a light-shielding layer by which the light-shielding layer having superior definition and light-shielding properties may be easily formed with sufficient accuracy, and which may be particularly useful for forming a color filter, and a substrate having such light-shielding layer.

It is another object of the present invention to provide a method for forming a substrate having a light-shielding layer whereby the light-shielding layer having superior definition and light-shielding properties as well as low reflectance and electrical conductivity may be easily formed with sufficient accuracy by employing specified carbon black as the pigment.

It is a further object of the present invention to provide a counterelectrode substrate for a TFT array substrate for black and white display which is superior in definition and light-shielding properties and which may be formed by a simplified process, and a liquid crystal display device (LCD) for black and white display employing the counterelectrode substrate.

According to the present invention, there is provided a method for preparing a substrate having a light-shielding layer comprising the steps of i) forming a positive photosensitive coating film on a transparent electrically conductive layer formed on a transparent substrate, ii) exposing the positive photosensitive coating film via a mask exhibiting light transmitting properties only at portions thereof registering with the light-shielding layers iii) removing and developing the portions of the coating film exposed to light for exposing the transparent electrically conductive layer and electrodepositing a dark-hued coating on at least a portion of the exposed transparent electrically conductive layer for forming the light-shielding layer, and iv) heating the light-shielding layer.

According to the present invention, there is also provided a method for preparing a substrate having a light-shielding layer comprising the steps of i) forming a negative photosensitive coating film on a transparent electrically conductive layer formed on a transparent substrate, ii) exposing the negative photosensitive coating film via a mask exhibiting light transmitting properties only at portions thereof other than those registering with the light-shielding layer, iii) removing and developing the portions of the coating film not exposed to light for exposing the transparent electrically conductive layer and electrodepositing a dark-hued coating on at least the exposed transparent electrically conductive layer for forming the light-shielding layer, and iv) heating the light-shielding layer.

According to the present invention, there is also provided a substrate having a light-shielding layer comprising a transparent substrate, a transparent electrically conductive layer formed on the transparent substrate and a light-shielding layer formed on the transparent electrically conductive layer, wherein the light-shielding layer contains carbon black having a maximum particle size of 1 μm or less dispersed within a polymer matrix and wherein the light-shielding layer has a volume resistivity of 1×10^2 ohm·cm or higher.

According to the present invention, there is provided a liquid crystal display device for black and white display comprising a first polarizing plate, a substrate arranged on the first polarizing plate, a thin film transistor, and a pixel electrode driven by the thin film transistor, the thin film transistor and the pixel electrode both being formed on an

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outer surface of the substrate opposite to the first polarizing plate, an inner alignment layer in contact with the thin film transistor and the pixel electrode, a liquid crystal layer being in contact with the inner alignment layer and having an outer alignment layer on its opposite side surface, a second polarizing plate arranged on an outermost side surface of the display device and a counterelectrode substrate arranged between the outer alignment layer and the second polarizing plate, the counterelectrode substrate having a transparent substrate in contact with the second polarizing plate and a transparent electrically conductive layer electrodeposited on the other side of the transparent substrate, a light-shielding layer of a dark-hued colored layer formed on the electrically conductive layer being contacted with the outer alignment layer.

BRIEF DESCRIPTION OF THE DRAWING

The sole figure is a schematic cross-sectional view for a black and white liquid crystal display device according to the present invention.

DESCRIPTION OF THE INVENTION

The present invention will be explained in detail hereinbelow.

With the method of the present invention, the step of forming a positive photosensitive coating film on a transparent electrically conductive layer (transparent electrode) on the transparent substrate, referred to hereinafter as a step 1-A, is first performed. Alternatively, with the method of the present invention, the step of forming a negative photosensitive coating film on a transparent electrically conductive layer on the transparent substrate, referred to hereinafter as a step 1-B, is first performed.

There is no limitation to the materials of the transparent substrate, provided that it is transparent and plate-shaped. Specifically, these materials may include quartz, various glasses, various transparent resins (plastics), such as polyester, polyphenylene sulfide, epoxy resins, acrylic resins, polymethylpentene, polyimides, polycarbonates, polyamides, polysulfone, polyether, polystyrene, acrylonitrile-styrene copolymers or cellulose triacetate. In view of the properties desired of the color filter and so forth, as an ultimate product, the surface of the transparent substrate is desirably smooth and occasionally ground before use.

The transparent electrically conductive layer formed on the transparent substrate is preferably formed of tin oxide, indium oxide, indium-tin oxide or antimony oxide, and usually has a film thickness of 20 to 300 nm. The transparent electrically conductive layer may be formed by spraying, chemical vapor deposition (CVD), sputtering or vacuum evaporation.

There is no particular limitation to the photoresist forming the positive photosensitive coating film, provided that the light exposed portion is soluble in a developing solution and thereby removed. The photoresist may be enumerated by compounds containing quinone diazido groups, compounds having diazomeldrum's acid or nitrobenzyl esters, a composition containing these compounds, and chemically amplified compositions employing a compound generating an acid by light (acid-generating agent by light). More specific examples include a composition prepared by suitably mixing with a resin having a film-forming function a reaction product between a compound having a hydroxyl group and a quinone diazidosulfonic acid derivative or a quinonediazido compound having an isocyanate group. There is no

limitation to the mixing ratio which may be suitably selected depending on conditions of the light exposure and development. Examples of the photoresist may further include chemically amplified compositions composed of a resin having a quinonediazido group or a composition containing a resin having a quinonediazido group, an acid-generating agent by light selected from aryl sulfonium salts, aryl iodonium salts, halomethyl triazine, esters of sulfonic acid and tosylates having an o-nitrobenzyl group, and polyhydroxystyrene having a t-butoxycarbonyl group or a tetrahydropyranyl group introduced therein. Various commercially available positive photoresists may also be employed.

There is no limitation to the photoresist forming the negative photosensitive coating film, provided that the light exposed portion thereof is not removed by a developing solution and only the unexposed portion thereof is insoluble in the developing solution. For example, a prepolymer or a resin having the molecular weight ranging in general between 500 and 10,000 and containing an ethylenic double bond capable of being cross-linked by light, such as (meth)acryloyl group, e.g. acryloyl or methacryloyl group, and/or cinnamoyl group, in its molecule, which prepolymer or resin may be dissolved or dispersed in water along with a photopolymerization initiator and occasionally with a dye and/or a pigment.

The prepolymer or the resin may be enumerated by the prepolymers, such as epoxy (meth)acrylate, urethane (meth)acrylate or polyester (meth)acrylate; cationic resins which are produced by introducing onium groups, such as amino groups, ammonium or sulfonium and the above-mentioned photosensitive groups into acrylic resins, epoxy resins, urethane resins or polybutadiene resins and which are dissolved and/or dispersed in an organic solvent or solubilized and/or dispersed in water with acids such as formic acid, acetic acid, propionic acid or lactic acid or with acidic substances; and anionic resins which are produced by introducing carboxyl groups and the above-mentioned photosensitive groups into acrylic resins, polyester resins, maleinated oil resins, polybutadiene resins or epoxy resins, and which are dissolved and/or dispersed in an organic solvent or solubilized and/or dispersed in water with basic substances such as triethylamine, diethylamine or ammonia. Prepolymers or resins capable of being solubilized and/or dispersed in water are especially preferred for simplifying the process or preventing environmental pollution.

Low molecular (meth)acrylates may be added to the negative photosensitive coating material for adjusting the viscosity and photosensitivity of the coating film. These (meth)acrylates may be enumerated by 2-hydroxyethyl (meth)acrylate, 2-phenoxyethyl (meth)acrylate, 3-phenoxy-2-hydroxypropyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, tricyclodecane (meth)acrylate, hexanediol di(meth)acrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, dipentaerythritol hexaacrylate and tris(acryloyloxyethyl) isocyanurate. These may also be used in a mixture. The mixing ratio of these (meth)acrylates is preferably 0 to 50 parts by weight and more preferably 0 to 30 parts by weight to 100 parts by weight of the resin for the negative photosensitive coating material. If the mixing ratio exceeds 50 parts by weight, the coating film undesirably tends to be viscous.

As the photopolymerization initiator, any material known in the art may be employed. Examples of the known photopolymerization initiator include benzoin and ethers thereof, benzyl alkyl ketals, benzophenone derivatives, anthraquinone derivatives and thioxanthone derivatives. The photopolymerization initiator may be admixed with a suit-

able sensitizer if so desired. The photopolymerization initiator is added preferably in an amount of 0.1 to 30 parts by weight and more preferably in an amount of 0.5 to 20 parts by weight to 100 parts by weight of the resin for the negative photosensitive coating material. If the photopolymerization initiator is added in the amount less than 0.1 part by weight, photocurability becomes insufficient. If it exceeds 30 parts by weight, curing proceeds excessively so that the film strength becomes insufficient with economic demerits.

10 The negative photosensitive coating material may be prepared by a method comprising mixing a resin for the photosensitive coating material, a photopolymerization initiator, an organic solvent and/or water and, if necessary, various assistant agents, such as dyes and/or pigments, acidic or basic substances, dispersion assistant agents for dyes or pigments, levelling agents for improving smoothness of the coating films, viscosity adjustment agents or anti-foaming agents, and sufficiently dispersing the ingredients, using a well-known dispersion means, such as a sand mill or an attriter.

15 There is no particular limitation to the organic solvents employed for dispersing or dissolving the above-mentioned positive or negative photoresists or compositions thereof capable of forming the photosensitive coating films. Examples of the solvents may include glycolethers, such as

20 ethylene glycol monobutylether, ethylene glycol monohexylether, ethylene glycol monophenylether, propylene glycol monomethyl ether, propylene glycol monophenylether, diethylene glycol dimethylether or triethylene glycol dimethylether; ketones, such as acetone, methylethyl ketone, methylisobutyl ketone, cyclohexanone, isophorone, or N-methyl pyrrolidone; ethers, such as dibutyl ether, dioxane, or tetrahydrofuran; alcohols, such as methoxybutanol, diacetone alcohol, octanol, butanol, or isopropanol; hydrocarbons, such as toluene, xylene, cyclohexane or hexane; esters, such as ethyl acetate, butyl acetate, 2-methoxy ethyl acetate, 2-methoxy propyl acetate or ethyl benzoate; and acid amides, such as dimethyl formamide, N,N-dimethyl acetamide or dimethyl sulfoxide. These organic solvents may be used alone or in combination.

25 30 35 40 The positive photosensitive coating film or the negative photosensitive coating film may be formed on the transparent electrically conductive layer by any known methods, such as immersion, spraying, spin coating, roll coating, screen printing or electrodeposition.

45 There is no particular limitation to the film thickness of the photosensitive coating film, which may be suitably selected depending on the properties required of the color filter as the ultimate product. Above all, in relation to the shape of the light-shielding layer, it is desirable for the film thickness of the photosensitive coating film to be usually 0.5 to 20 times and preferably 1 to 10 times that of the light-shielding layer. If the film thickness of the photosensitive coating film is less than the above range, there may be a large possibility that the thick-colored layer which is to form the light-shielding layer by electrodeposition during the next step is formed on the photosensitive coating film, or the light-shielding layer is formed which has a line width broader than that of the pattern prescribed by the photosensitive coating film. If the film thickness of the photosensitive coating film is larger than the above range, there may be a high possibility that problems are presented in the resolution of the photosensitive coating film or the electrodeposition or the coating material for electrodeposition can hardly enter the opening during electrodeposition so that the light-shielding layer cannot be formed in a desired manner.

50 55 60 65 65 For adjusting the film thickness, the coating conditions may suitably be selected depending on the particular coating

method. In the case of spin coatings for example the film thickness can easily be controlled by adjusting the viscosity of the coating liquid or the number of revolutions of a spinner, while in case of electrodeposition, for example the conditions of electrodeposition such as coating voltage, electrodeposition time or liquid temperature may be changed to adjust the film thickness.

In the method of the present invention, the positive photosensitive coating film is exposed to light via a mask exhibiting light-transmitting properties only at portions thereof registering with the light-shielding layer. The process step is referred to hereinafter as a step (2-a). Alternatively, the negative photosensitive coating film is exposed to light via a mask exhibiting light-transmitting properties only at portions thereof other than those registering with the light-shielding layer. The process step is referred to herein-after as a step (2-b).

The mask exhibiting light transmitting properties at the portions thereof registering with the light-shielding layer, or the mask exhibiting light transmitting properties at the portions thereof other than those registering with the light-shielding layer, is a photomask usually employed in photolithography, and needs only to be patterned to have a desired shape.

The light exposure may be effected using a light source capable of generating a large quantity of ultraviolet rays, such as a high-pressure mercury lamp, an ultra-high pressure mercury lamp, xenon lamp, a metal halide lamp, an excimer laser or a synchrotron light radiator. If necessary, a radiation source other than the ultraviolet ray generator may be employed. The light exposure conditions may be suitably selected depending on the photosensitive coating film, the method or the apparatus for light exposure. For example, there is no particular limitation to the amount of light exposure which may be suitably selected depending on the light source or the photosensitive coating film. The amount of light exposure is usually 0.1 to 1000 mJ/cm² and preferably 5 to 500 mJ/cm².

With the method of the present invention, when the positive photosensitive coating film is employed, the portions of the coating film exposed to light are removed and developed for laying or exposing the transparent electrically conductive layer to the outside, and a dark-hued coating is electrodeposited on at least the exposed transparent electrically conductive layer said to the outside for forming the light-shielding layer. The above process step is referred to hereinafter as the step (3-a). With the method of the present invention, when the negative photosensitive coating film is employed, the portions of the coating film not exposed to light are removed and developed for laying or exposing the transparent electrically conductive layer to the outside, and a dark-hued coating is electrodeposited on at least the exposed transparent electrically conductive layer laid to the outside for forming the light-shielding layer. The above process step is referred to hereinafter as the step (3-b).

There is no particular limitation to the development conditions in the steps (3-a) or (3-b) and any conditions may be suitably employed depending on the amount of light exposure in the steps (2-a) or (2-b), solubility of the photosensitive coating film in the developing solution, the kind or the concentration of the developing solution, the developing time or developing temperature. There is no particular limitation to the developing solution if it is capable of removing the exposed or unexposed portions of the photosensitive coating film of the step (3-a) or (3-b) by development, such that the developing solution may be suitably

selected depending on the types or the light exposed state of the photosensitive coating film.

In the step (3-a), an aqueous solution of a basic substance is usually employed as the developing solution. Examples of the basic substance include sodium carbonate, sodium hydrogen carbonate, sodium metasilicate, tetraalkyl ammonium hydroxide, such as tetramethyl ammonium hydroxide, sodium hydroxide, potassium hydroxide or ammonia. For the developing solution, an organic solvent, such as alcohols, glycol ethers, ketones, hydrocarbons or chlorinated hydrocarbons, may be employed either as a mixture or in combination with the above-mentioned aqueous developing solutions. Of these, the aqueous developing solution is preferred.

If a cationic resin is used as an ingredient of the photosensitive coating material, the developing solution employed in the step (3-b) may be an aqueous solution containing an acidic substance dissolved therein. The acidic substance may be enumerated by organic acids, such as formic acid, acetic acid, propionic acid or lactic acid, and inorganic acids, such as hydrochloric acid or phosphoric acid. If an anionic resin is used as an ingredient of the negative photosensitive coating material, a developing solution containing a basic substance dissolved in water may be employed. The basic substance includes sodium carbonate, sodium hydrogen carbonate, sodium metasilicate, tetraalkylammonium hydroxide, sodium hydroxide and potassium hydroxide. As the developing solution, an organic solvent, such as alcohols, glycol ethers, glycols, ketones, hydrocarbons or chlorinated hydrocarbons may be employed, either as a mixture or in combination with the aqueous developing solution. The developing solution may be admixed with surfactants or anti-foaming agents for improving wettability or anti-foaming properties. An aqueous developing solution is preferably employed in view of toxicity or working environments.

If the aqueous solution of tetramethyl ammonium hydroxide is used in the step (3-a) for the developing solution, the developing conditions may be suitably selected from the concentration of 0.01 to 20 wt %, and preferably 0.05 to 10 wt %, the temperature of 10° to 80° C. and preferably 15 to 40° C., the developing time of 2 to 600 seconds and preferably 4 to 300 seconds.

If an aqueous solution of sodium carbonate is used as the developing solution in the step (3-b), the concentration of sodium carbonate may usually be in a range of 0.01 to 25 wt % and preferably in a range of 0.05 to 15 wt %, the temperature may be in a range of 10° to 70° C., and the developing time may be suitably selected from a range of 5 to 600 seconds and preferably from a range of from 5 to 300 seconds. If an aqueous solution of lactic acid is used in the step (3-b), the concentration of lactic acid may usually be in a range of 0.01 to 50 wt % and preferably in a range of 0.05 to 25 wt %, the temperature may be in a range of 10° to 70° C. and preferably in a range of 15° to 50° C., and the developing time may be suitably selected from a range of 2 to 600 seconds and preferably from a range of from 4 to 400 seconds.

The dark-hued colored coating material employed in the step (3-a) or (3-b) may be exemplified by a water-soluble or -dispersible coating material containing (a) a dye and/or a pigment having a thick hue, such as black, thick indigo or thick brown, (b) a binder resin for electrodeposition and occasionally (c) a curing agent.

The dye and/or the pigment may be exemplified by, for example, carbon black, graphite, vanadium trioxide, manganese dioxide, molybdenum disulfide, triiron tetroxide,

Aniline Black, Sudan Black B, Acid Black 1 and 52, Fast Black K Salt, Nigrosin or mixtures thereof. The dyes and/or pigments shown in detail in "COLOR INDEX", third issue, may also be employed.

If the substrate having the light-shielding layer formed by the method of the present invention is employed as the black matrix for the color filter, there is no particular limitation to the dyes and/or the pigments and any dyes and/or pigments enumerated above may be employed. If the substrate having the light-shielding layer formed by the method of the present invention is employed as the light-shielding layer for the counterelectrode substrate for a TFT array substrate for black and white display, there is also no particular limitation to the dye and/or pigment contained therein and any of the above-enumerated dyes and/or pigments may be employed. Of these, however, the pigments, above all, those in the form of electrically conductive fine particles, are particularly preferred. As the electrically conductive fine particles, at least one of carbon black, metal oxides, such as tin oxide, ITO, indium oxide, titanium oxide, ruthenium oxide, or vanadium oxide, and metals, such as gold, platinum, palladium, silver alloys, copper or nickel, may preferably be employed. Needless to say, two or more of these components may be used as a mixture in order to strike a balance between light-shielding properties and electrical conductivity. It is preferred for the substrate having the light-shielding properties of the present invention to have the volume resistivity of 1×10^2 ohm·cm or higher and above all the volume resistivity of 1×10^2 to 1×10^{12} ohm·cm and the surface resistivity of 1×10^2 to 1×10^{14} ohm/□. If the volume resistivity is lower than 1×10^2 ohm·cm, the dye and/or the pigment tends to be raised in concentration such that a film having satisfactory physical properties, and above all high adherence cannot be produced. If the volume resistivity is higher than 1×10^{12} ohm·cm, the dye and/or the pigment tends to have low concentration, thus leading to insufficient light-shielding properties. Similarly, if the surface resistivity is lower than 1×10^2 ohm/□, the dye and/or the pigment tends to be raised in concentration and hence poor in adherence, whereas, if the surface resistivity is higher than 1×10^{14} ohm/□, sufficient light-shielding properties occasionally cannot be achieved.

If the black matrix portion of the light-shielding layer is used as a counterelectrode substrate for a TFT array substrate for black and white display, light modulation due to the liquid crystal orientation on the black matrix has the effect of preventing light leakage, so that higher electrical conductivity of the black matrix portion, that is the light-shielding portion, is desired. Specifically, the volume resistivity of 1×10^2 to 1×10^9 ohm·cm and preferably 1×10^2 to 1×10^6 ohm·cm and the surface resistivity of 1×10^2 to 1×10^9 ohm/□ and preferably 1×10^2 to 1×10^6 ohm/□ is desired. If the volume resistivity is lower than 1×10^2 ohm·cm, the electrically conductive fine particles usually need to be used in a higher concentration, which leads undesirably to inferior adhesivity of the light-shielding layer to the ITO substrate. If the volume resistivity is larger than 1×10^9 ohm·cm, the liquid crystal display device becomes undesirably inferior in viewing properties. If the surface resistivity is lower than 1×10^2 ohm/□, the electrically conductive fine particles usually need to be used in a higher concentration, which leads undesirably to inferior adhesivity of the light-shielding layer to the ITO substrate. If the surface resistivity is larger than 1×10^9 ohm/□, the liquid crystal display device may lack viewing properties. The lowering of viewing properties is due to the fact that the liquid crystal in contact with the light-shielding layer is not responsive to the voltage appli-

cation. That is, the TFT-LCD is usually employed with normally white so that the light polarized by the polarizing plate undergoes birefringence at the liquid crystal in contact with the light-shielding layer, thus undesirably leading to light leakage in the vicinity of the pixels and hence to lowered contrast and inferior viewability of the liquid crystal display device. Accordingly, in the black matrix of the present invention, it is not necessary to further form an ITO relative to the black matrix.

If, on the other hand, the black matrix is used as the light-shielding layer of the color filter for the liquid crystal display device manufactured by the electrodeposition method, it is preferred for the black matrix portion to have low electrical conductivity in order to prevent the occurrence of the phenomenon of electrodeposition of the electrodeposited layers of, for example, R, G and B on the black matrix portion.

Specifically, it is desirable for the black matrix portion of the light-shielding layer to have the volume resistivity of 1×10^6 to 1×10^{12} ohm·cm and the surface resistivity of 1×10^4 ohm/□ to 1×10^{14} ohm/□. If the volume resistivity is lower than 1×10^6 ohm·cm, the phenomenon of over-coating, that is the phenomenon of the colored coating material being electrodeposited on the light-shielding layer undesirably tends to be produced. Above the volume resistivity of 1×10^{12} ohm·cm, light-shielding properties are extremely lowered, thus leading to lowered contrast of the color filter and lowered protective characteristics of TFT. Below the surface resistivity of 1×10^4 ohm/□, the phenomenon where the colored coating material may be electrodeposited on the light-shielding layer (over-coating) may occur. If the surface resistivity is higher than 1×10^{14} ohm/□, the light-shielding properties are significantly lowered, so that characteristics of the color filter, such as contrast, or protective characteristics of the TFT, are undesirably lowered.

Of the above pigments, carbon black is preferred because it exhibits high light-shielding properties even if used in small quantities. In view of light-shielding properties and stability of the electrodeposition coating material, it is necessary for the carbon black to have the maximum particle size of not larger than 1 μm. As for the maximum particle size of the carbon black on dispersion thereof, as measured by the light-scattering particle size distribution measurement device manufactured by OTSUKA ELECTRONICS CO., LTD. under the trade name of "PAR-III", the number average particle size (dn) is desirably not more than 1 μm and more desirably not more than 0.5 μm, while the weight average particle size (dr)/number average particle size (dn) is desirably not more than 2.5. It is more preferred for dn and the ratio dv/dn to be not more than 0.3 Nm and not more than 2, respectively. If the maximum particle size exceeds 1 μm, the electrodeposition coating material tends to be inferior in stability, while the resulting light-shielding layer tends to be inferior in smoothness or definition. The maximum particle size of not more than 1 μm is desirable because the electrical conductivity of the light-shielding layer becomes more readily controllable by suitably selecting the pigment/binder resin mixing ratio or the heat treatment conditions as later explained.

In general, if the electrically conductive material, such as carbon black, is used as a pigment in a dark-hued coating material, the dark-hued layer exhibits electrical conductivity. It is possible with the present invention to increase the electrical conductivity of the dark-hued layer to such an extent that the light-shielding layer can be utilized as the counterelectrode for a TFT array substrate, or to decrease the electrical conductivity of the dark-hued layer to such an

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extent that the light-shielding layer can be satisfactorily employed as a light-shielding layer for the color filter manufactured by the electrodeposition method. The black-hued black matrix exhibiting high light-shielding properties may be produced if the above-mentioned dye and/or the pigment is used in an amount usually of 2 to 300 parts by weight and preferably 3 to 100 parts by weight to 100 parts by weight of the electrodeposition binder resin.

If carbon black is employed as the pigment, it is possible to accord stability and reliability to the light-shielding layer on curing by heating and hence to produce the black-hued black matrix exhibiting light-shielding properties by employing usually 10 to 80 parts by weight and preferably 20 to 60 parts by weight of the carbon black to 100 parts by weight of the electrodeposition binder resin. The black matrix in which carbon black is dispersed in this manner in the polymer matrix exhibits light reflectance which is lower than when the black matrix is manufactured by metal sputtering or the like.

For producing a counterelectrode for a TFT array substrate for black and white display using carbon black, the electrically conductive fine particles are preferably added in an amount of 30 to 80 parts by weight to 100 parts by weight of the electrodeposition binder resin. If the particles are added in an amount less than 30 parts by weight, the resulting black matrix is low in light-shielding properties and electrical conductivity, whereas, if the particles are added in an amount exceeding 80 parts by weight, the resulting black matrix is lowered in planarity and definition.

As the above-mentioned electrodeposition binder resin, the resins having groups which become cationic or anionic groups when dissolved and/or dispersed in water may be employed. If a transparent substrate having an ITO transparent electrically conductive layer thereon is used as the substrate for electrodeposition, it is not desirable to perform cationic electrodeposition using a resin containing the groups which become cationic groups, because the ITO layer becomes oxidized by the acid contained in the electrodeposition solution. Thus it is preferred to perform anionic electrodeposition using a resin containing the groups which become anionic groups. If cationic electrodeposition is to be performed, a substrate which is not oxidized with the acid contained in the electrodeposition solution, such as stainless steel or platinum, needs to be employed, and the light-shielding layer produced by electrodeposition needs to be transferred onto an actually employed transparent substrate, such as glass. As the resins containing cationic groups, those produced by introducing amino groups or onium groups, such as ammonium, sulfonium or phosphonium, into acrylic, epoxy, urethane, polybutadiene of polyamide resins and rendering the resulting material soluble or dispersible in water with acids such as formic acid, acetic acid, propionic acid or lactic acid, or with acidic substances.

The anionic resins may be enumerated by, for example, acrylic resin, polyester resin, maleinated oil resin, polybutadiene resin or epoxy resin containing carboxyl groups and rendered soluble or dispersible in water with basic substances, such as triethylamine, diethylamine, dimethylethanolamine or ammonia. The curing agents, which may be occasionally employed, may be suitably selected in view of suitability of addition thereof to the electrodeposition binder resin employed, and may be enumerated by, for example, melamine, benzoguanamine, urea, or derivatives thereof; amino resins, such as melamine or urea resins; phenolic resins; and blocked isocyanates. Those curing agents which remain effective at lower temperatures are preferably employed. The dark-hued coating material may further be

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admixed with dispersion assistant agents for dyes or pigments, or various assistant agents, such as levelling agents for improving smoothness of the coating film, viscosity controllers or anti-foaming agents.

The dark-hued coating material may be produced by mixing the dye and/or the pigment, the composition containing the electrodeposition binder and, if necessary, the curing agent, organic solvent, water, acidic substances, basic substances, dispersion assistant agents for the dye or the pigment, levellers, viscosity controllers and the anti-foaming agents, sufficiently dispersing the mixture using commonly employed dispersing means, such as sand mills, roll mills, attritors or ball mills, and diluting the resulting dispersion with water to preferably a pre-set concentration such as approximately 4 to 25 wt % and more preferably 7 to 20 wt % of solid contents to give a coating material suited for electrodeposition. An organic solvent employed for dispersion and dissolution of the resin for the photosensitive coating film may be suitably selected and employed for facilitating the dissolution and/or dispersion of the binder for electrodeposition or improving bath stability or with a view to producing a smooth coating film.

There is no limitation to the thickness of the dark-hued layer, that is the light-shielding layer, formed by electrodeposition coating, such that it may be suitably selected depending on the properties demanded of the color filter or the designing of the display device. In view of light-shielding properties, the dry thickness of the light-shielding layer is usually 0.3 to 5 µm and preferably 1 to 3 µm. The thickness of the light-shielding layer may be selected from one coating material to another because it is varied depending on the kind and the size of the dye and/or pigment employed or the mixing ratio of the electrodeposition binder resin. The film thickness may be controlled by adjusting the conditions of electrodeposition, such as coating voltage, electrodeposition time or liquid temperature.

The conditions of electrodeposition coating for forming the dark-hued layer, such as voltage, electrodeposition time or liquid temperature, may be suitably selected depending on the kind of the dark-hued coating material or the thickness of the desired light-shielding layer. For example, the coating voltage may usually be a dc voltage of 5 to 500 V, preferably 10 to 300 V and more preferably 10 to 150 V, while the electrodeposition time is usually 5 to 300 seconds and preferably 10 to 200 seconds and the liquid temperature is 10° to 35° C. and preferably 15° to 30° C. Preferably, the current supply is discontinued after lapse of the electrodeposition time necessary to obtain the desired film thickness, the substrate is taken out of the bath, freed of any excess bath liquid by washing with water and dried.

With the method of the present invention, the dark-hued coating electrodeposited on the substrate, that is the light-shielding layer, is heated, referred to hereinafter as the step (4).

The heating may be carried out under such conditions as will permit the moisture in the light-shielding layer formed by electrodeposition of the steps (3-a) or (3-b) to be dried easily. If the resin for electrodeposition exhibits heat curability, the curing by heating may be carried out under such condition as will permit cross-linking reaction to be completed depending on the objective. Since the resistance to the developing solution and to alkali of the light-shielding layer may be influenced by, for example, the concentration of the acids contained in the coating film constituting the light-shielding layer, the heat treatment does not solely depend on its conditions.

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If the light-shielding layer is not required to exhibit resistance to the developing solution or to alkali, or if the electrical conductivity of the light-shielding layer needs to be as low as possible, the heat treatment may be carried out at a temperature of, for example, not higher than 150° C., preferably 80° to 140° C., usually for 0.5 minute to one hour and preferably for 1 to 30 minutes. By using these conditions, it is possible for the light-shielding layer to have practically acceptable electrical insulating properties, such as the volume resistivity of 1×10^6 to 1×10^{12} ohm-cm and the surface resistivity on the order of 1×10^4 to 1×10^{14} ohm/□, even although the light-shielding layer is formed of carbon black and in case where colored layers of R, G and B are to be subsequently electrodeposited.

If the light-shielding layer requires to exhibit resistance to the developing solution or to alkali, and if electrical conductivity is to be as high as possible, heating may be carried out at a temperature of, for example, 130° to 270° C., preferably 140° to 250° C., for a time period usually employed for such heating. These conditions for heating may be suitably selected depending on whether the light-shielding layer formed in accordance with the present invention is employed for a black matrix for a color filter or for a black matrix for a counterelectrode for a TFT array substrate for black and white display. That is, when the black matrix for the color filter is formed using carbon black as the pigment and, in succession thereto, the colored layers of red, blue and green hued layers are formed by electrodeposition, it is preferred to carry out the heating under such conditions as will permit the moisture on the surface of the light-shielding layer formed by electrodeposition of the step (3-a) or (3-b) to be dried readily. It is preferred to carry out the curing by heating under such condition as will maintain electrical insulating properties inhibiting the electrodeposition of the colored layer on the black matrix, that is, under the conditions of the temperature of not higher than 180° C. and preferably 80 to 140° C. and the heating time of 2 to 120 minutes. The electrical insulating properties in terms of the volume resistivity of 1×10^6 ohm-cm or higher, as stated previously, is desirable. Although the moisture is sufficiently dried with the temperature exceeding 180° C., the volume resistivity becomes less than 1×10^6 ohm-cm when the carbon black proportion satisfying the requirements for light-shielding properties is used, so that the colored layer is undesirably formed on the black matrix in the course of the formation of the colored layer by electrodeposition.

If the colored layer is formed by electrodeposition, it is crucial to control the electrical conductivity of the light-shielding layer in order to prevent over-coating of the colored layer. There is no problem when forming the colored layer by the pigment-dispersing method or the printing method, in which cases the heating of the light-shielding layer may be usually at 80° to 270° C. and preferably at 130° to 250° C.

When employing the black matrix of the light-shielding layer for the counterelectrode for a TFT array substrate for black and white display, it is preferred for the black matrix to have the electrical conductivity acceptable in view of the function of the counterelectrode. For example, the heating may be carried out usually at 130° to 350° C., preferably at 140° to 280° C., usually for 5 minutes to 3 hours, preferably for 10 minutes to 1.5 hours. In such case, a light-shielding layer having the volume resistivity on the order of 1×10^2 to 1×10^9 ohm-cm may be produced. The counterelectrode having such black matrix needs to have some electrical conductivity because the liquid crystal on the black matrix has to be responsive to the voltage application. The electrical

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properties of the light-shielding layer may be controlled depending on the kind of the electrically conductive fine particles, the mixing ratio of the electrically conductive fine particles to the binder resin for electrodeposition or the conditions of the heating. It suffices if the black matrix after heating exhibits the volume resistivity of 1×10^2 to 1×10^9 ohm-cm, preferably 1×10^2 to 1×10^6 ohm-cm.

In addition, the electrical conductivity of the light-shielding layer may be controlled more extensively by selecting not only the conditions of heating but also the proportion of the carbon black in the materials of the light-shielding layer within the above-mentioned range. In this case, it desirably becomes possible to select the volume resistivity in the range of from 1×10^2 to 1×10^{12} ohm-cm and the surface resistivity in a range of from 1×10^2 to 1×10^{14} ohm/□, as measured at 20° and 60% RH, depending on the usage and application.

The present invention is also directed to a substrate having a light-shielding layer in which the carbon black having the maximum particle size of not more than 1 μm is dispersed in the polymer matrix and in which the light-shielding layer has the volume resistivity of not less than 1×10^2 ohm-cm and is formed on the transparent electrically conductive substrate. Although the light-shielding layer is produced most preferably by the above-mentioned method, it may also be produced by a method of forming the light-shielding layer on the patterned transparent electrically conductive substrate by electrodeposition, a method of printing the light-shielding layer on the patterned transparent electrically conductive substrate, or a photolithographic method. Of these, the photolithographic method resides in applying the light-shielding resin composition exhibiting photocurability on a substrate and drying the resin composition followed by light exposure and development.

Referring to the drawings an embodiment of a counterelectrode substrate for a thin film transistor (TFT) array substrate for black and white display, and a liquid crystal display device for black and white display having the counterelectrode substrate incorporated therein, is hereinafter explained.

A liquid crystal display device 10 for black and white display includes a TFT array substrate 12 for black and white display, a counterelectrode substrate 13 and a liquid crystal layer 11 sandwiched between the substrates 12 and 13. The TFT array substrate 12 is made up of thin film transistors (TFTs) 12b and pixel electrodes 12c driven by the TFTs, source bus lines 12d and gate bus lines (not shown) arranged on a transparent substrate 12a. These components are covered by an inner alignment layer 12e as shown. The counterelectrode substrate 13 is made up of a transparent substrate 13a, a transparent electrically conductive layer 13b formed on the transparent substrate 13a and a light-shielding layer 13c formed by electrodeposition coating of the dark-hued coating material. These components are covered by an outer alignment layer 13d. Polarizing plates 14, 15 are mounted on the transparent substrates 12a, 13a, respectively.

It is possible with the method of the present invention to produce a light-shielding layer having high definition and light-shielding capability and low light reflectance easily and with a high accuracy, and may be applied in particular to the preparation of a color filter for a liquid crystal display device or the like having superior properties.

With the present invention, there may also be provided a counterelectrode substrate for a TFT array substrate for black and white display, having a black matrix excellent in

definition and light-shielding properties, and a TFT liquid crystal display device for black and white display employing the counterelectrode substrate. The present invention renders it possible to simplify the production process as compared to the conventional photolithographic production process.

TABLE 2

Coating No. Color	Y-1 Black	Y-2 Red	Y-3 Green	Y-4 Blue
<u>Particle size (μm)</u>				
Medium size	0.165	0.171	0.176	0.158
Maximum particle size	0.34	0.39	0.39	0.39

EXAMPLES OF THE INVENTION

The present invention is now explained with reference to Examples, Comparative Examples and Application Examples. However, these Examples are given only by way of illustration and are not intended for limiting the invention.

Synthesis Example 1

Preparation of Black-Hued Coating Material (Y-1) and Colored Coating Materials (Y-2, Y-3 and Y-4)

An acrylic resin manufactured by TOA GOSEI CHEMICAL INDUSTRY CO., LTD. under the trade name of "ARON S-4030" was neutralized with triethylamine to pH of approximately 8 and admixed with deionized water to give an aqueous resin solution (S).

To the aqueous resin solution (S), carbon black, azo metal salt red pigment, Phthalocyanine Green and Phthalocyanine Blue were added under agitation to prepare black-hued, red-hued, green-hued and blue-hued liquid pigment dispersions.

By a separate process, the above-mentioned acrylic resin is mixed with a melamine resin manufactured by SUMITOMO CHEMICAL CO., LTD. under the trade name of "SUMIMAL M-66B" and neutralized to pH of approximately 8 with triethylamine. The neutralized mass was then admixed with deionized water to prepare an aqueous resin solution (T).

The aqueous resin solution (T) was added to each of the respective hued pigment dispersions to produce a black-hued coating material (Y-1) and other hued coating materials (Y-2, Y-3 and Y-4) having the compositions shown in Table 1. The resulting coating materials were thermosetting and exhibited anionic electrodeposition properties. The particle size distribution of the resulting coating materials was measured using a light-scattering particle size distribution measurement device manufactured by OTSUKA ELECTRONICS CO., LTD. under the trade name of "PAR-III". The results are shown in Table 2.

TABLE 1

Coating No. Color	Y-1 Black	Y-2 Red	Y-3 Green	Y-4 Blue
Acrylic resin (*1)	750.0	750.0	750.0	750.0
Melamine Resin (*2)	250.0	250.0	250.0	250.0
Triethylamine	61.8	61.8	61.8	61.8
Carbon black	333.3	—	—	—
Phthalocyanine Blue (*3)	—	—	—	300.0
Phthalocyanine Green (*4)	—	—	500.0	—
Azo metal salt red pigment (*5)	—	500.0	—	—

(*1) "ARON S-4030" (mfd. by TOAGOSE CHEMICAL INDUSTRY CO., LTD.)

(*2) "SUMIMAL M66B" (mfd. by SUMITOMO CHEMICAL CO., LTD.)

(*3) "SR-150C" (mfd. by SANYO SHIKISO KK)

(*4) "SAZ" (mfd. by SANYO SHIKISO KK)

(*5) "PIGMENT RED 4BS" (mfd. by SANYO SHIKISO KK)

Unit is gm.

Synthesis Example 2

Preparation of Dark-Hued Coating Materials (Y-5, Y-6 and Y-7)

In the aqueous resin solution (S) prepared by the Synthesis Example 1, fine powders of carbon black, antimony-containing tin oxide manufactured by CATALYSTS & CHEMICALS INDUSTRIES CO., LTD. under the trade name of "ELECOM TL-90", black-hued titanium oxide, manufactured by ISHIHARA SANGYO KAISHA, LTD. under the trade name of "S-1" and nickel manufactured by SUMITOMO METAL MINING CO., LTD. under the trade name of "ENP-005" were dispersed in pre-set amounts to prepare dark-hued coating materials.

The aqueous resin solution (T) prepared in Synthesis Example 1 was added to each of the dark-hued coating material to give respective hued coating materials shown in Table 3. The coating materials thus produced were thermosetting and exhibited anionic electrodeposition properties.

TABLE 3

Coating No.	Y-5	Y-6	Y-7
Acrylic resin	750.0	750.0	750.0
Melamine resin	250.0	250.0	250.0
Triethylamine	61.8	61.8	61.8
Carbon black	300.0	300.0	300.0
Sb-containing SnO ₂	33.3	—	—
Black titanium oxide	—	33.3	—
Nickel	—	—	33.3

Unit is gram.

Example 1

On a "CORNING 7059" glass (trade name) available from CORNING JAPAN KK, 1.1 mm thick, having an indium tin oxide (ITO) film, 100 nm thick, on its surface, referred to hereinafter as a master plate 1, a positive photoresist composed of a naphthoquinone diazido compound and a novolak cresol resin manufactured by TOKYO OHKA KOGYO CO., LTD. under the trade name of "OFPR-800", was applied by a spin-coating method to have a dry film thickness of 3 μm. The resulting product was irradiated by the light from an ultra-high pressure mercury lamp having a pre-set light-shielding pattern at 70 mJ/cm². After development with a 2.4 wt % aqueous solution of tetramethyl ammonium hydroxide, the positive photoresist at the exposed portion was selectively removed to lay an ITO film surface thereat to the outside. After washing with water and drying, a dc voltage of 25 V was applied at 25° C. for 60 seconds across the master plate 1 as an anode and a stainless steel beaker containing the black-hued coating material (Y-1) exhibiting anionic electrodeposition properties as a cathode, to perform electrodeposition. The master plate 1 was hoisted from the stainless steel beaker, washed with ion-exchanged water and dried at 70° C. for five minutes.

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After heating at 120° C. for 10 minutes, the entire surface of the master plate 1 was then irradiated with the light of the above-mentioned ultra-high pressure mercury lamp at 100 mJ/cm². The master plate 1 was developed with a 2.4 wt % aqueous solution of tetramethyl ammonium hydroxide. It was seen that no change was noticed in the black-hued electrodeposited layer and any residual positive photoresist was removed in its entirety. After washing with water and drying, the master plate 1 having the high-precision light-shielding layer having a film thickness of 2 μm was produced.

The surface resistivity of the coating film, as measured with a four-terminal method, using a surface resistance meter manufactured by MITSUBISHI PETROCHEMICAL CO., LTD. under the trade name of "LORESTA", was 6×10^6 ohm/□. The volume resistivity of the coating film, as measured using an impedance analyzer manufactured by OTSUKA ELECTRONICS CO., LTD., was 2×10^8 ohm·cm. The optical density of the coating film, as measured with a densitometer manufactured by KONICA CO. under the trade name of "KONICA DENSITOMETER PDA-65", was 3.30.

Example 2

The manufacture process of Example 1 was followed to form a high precision light-shielding layer followed by heating at 240° C for 60 minutes to prepare a master plate having a light-shielding layer having a film thickness of 2.0 μm. The surface resistivity, the volume resistivity and the optical density of the light-shielding layer were 1×10^2 ohm/μ, 1×10^3 ohm·cm and 3.3, respectively.

Example 3

The manufacture process of Example 2 was followed except that heating was performed at 180° C. for 10 minutes to prepare a master plate having a light-shielding layer having a film thickness of 2.0 μm. The surface resistivity, the volume resistivity and the optical density of the light-shielding layer were 2×10^3 ohm/□, 1×10^4 ohm·cm and 3.30, respectively.

Application Example 1

Using a master plate having a light-shielding layer obtained in Example 1, referred to hereinafter as the master plate 1, a color filter by the electrodeposition method as described hereinbelow was prepared.

A positive photoresist manufactured by TOKYO OHKA KOGYO CO., LTD. under the trade name of "OFPR-800" was applied by the spin coating method on the master plate 1 to give a dry film thickness of 3 μm. Then, using a photomask having a mosaic-shaped pattern in which the light exposure portions were larger vertically and horizontally by 10 μm than the gap between the light-shielding layers, light exposure and development were performed, for removing the portions exposed to light to thereby lay the ITO film thereat to the outside. Then, a dc voltage of 25 V was applied at 25° C. for 60 seconds across the master plate 1 as an anode and a stainless steel beaker containing the red-hued coating material (Y-2) exhibiting anionic electrodeposition properties as a cathode to perform the electrodeposition. The master plate 1 was hoisted from the stainless steel beaker, washed with ion-exchanged water and dried. The resulting master plate was then heat-treated at 120° C. for ten minutes to give a red-hued mosaic-shaped layer. Another mosaic-shaped layer neighboring the thus

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prepared mosaic-shaped layer was exposed to light and developed. The green-hued coating material (Y-3) was electrodeposited and heat-treated in the same way as for the red-hued coating material (Y-2). The operation was repeated for the blue-hued coating material (Y-4) for preparing a color filter. During the above-mentioned electrodeposition steps, the phenomenon of over-coating of the colored coating material on the light-shielding layer was not noticed. The developing liquid employed was a 1 wt % aqueous solution of sodium hydroxide containing 5 wt % of a surfactant manufactured by KAO CO., LTD. under the trade name of "PEREX NBL". For complete curing, the color filter was treated at 180° C. for 30 minutes to give a color filter having a black-hued light-shielding layer exhibiting high accuracy and superior transparency, uniformity and planarity.

Application Example 2

Using the master plate 1 having the light-shielding layer produced by the Example 1, a color filter was prepared in accordance with the pigment dispersion method as described hereinbelow.

Using a color mosaic system, manufactured by FUJI HUNT ELECTRONICS TECHNOLOGY KK under the trade name of "CR-2000", "CG-2000" and "CB-2000", red, green and blue hues were charged in the gaps between the light-shielding layers, in accordance with the processing method as designated by these systems for producing a color filter having excellent planarity. The photomask employed for light exposure had the light-transmitting portions equally dimensioned to the gaps between the light-shielding layers.

Example 4

Using a master plate having a light-shielding layer, obtained in Example 2, referred to hereinafter as a master plate 2, a TFT liquid crystal display device for black and white display was prepared. A display device having superior viewability was obtained.

Reference Example 1

A color filter was prepared in the same way as for the Example 4, using a master plate 2 having a light-shielding layer obtained in Example 2. While the red, green and blue hues were electrodeposited in the light-shielding layers, a color filter having only poor planarity could be obtained.

Comparative Example 1

Using the master plate 1 having the light-shielding layer prepared by the Example 1, a TFT liquid crystal display device for black and white display was prepared. The display device thus prepared was inferior in viewability.

Examples 5 to 7

A positive photoresist "OFPR-800" was coated by the spin coating method on each "CORNING 7059" glass employed in Example 1 (the master plate 1) to have a dry film thickness of 3 μm. Each of the master plates 1 was irradiated with light from an ultra-high pressure mercury lamp via a mask having a pre-set light-shielding pattern. After development with a 2.4 wt % aqueous solution of tetramethyl ammonium hydroxide, the positive photoresist was selectively removed at the exposed portion for laying the ITO film surface thereat to the outside. Then, a dc voltage of 25 V was applied at 25° C. for 60 seconds across each master plate 1 as an anode and each stainless steel

beaker containing each of the black-hued coating materials (Y-5, Y-6 and Y-7) exhibiting anionic electrodeposition properties as a cathode, to perform the electrodeposition. Each master plate 1 was hoisted from the stainless steel beaker, washed with ion-exchanged water and dried at 70° C. for five minutes.

The entire surface of each master plate 1 was then irradiated with light of the above-mentioned ultra-high pressure mercury lamp at 100 mJ/cm². After heating at 120° C. for 10 minutes, each master plate was developed with a 2.4 wt % aqueous solution of tetramethyl ammonium hydroxide. It was seen that no changes were noticed in the black-hued electrodeposited layers and any residual positive photoresist was removed in its entirety. After washing with water and drying, each master plate having the high-precision light-shielding layer having a film thickness of 2 μm was produced.

After drying, each master plate was cured by heating at 140° C. for 60 minutes to give a counterelectrode substrate for a TFT array substrate for black and white display. The surface resistivity, volume resistivity and OD values of the coating films obtained in this manner, are shown in Table 4.

TABLE 4

Example Coating No.	5 Y-5	6 Y-6	7 Y-7
Surface resistivity (Ω/□)	1×10^2	1×10^2	1×10^2
Volume resistivity (Ω · cm)	2×10^2	2×10^2	2×10^2
OD value	8.0	8.0	8.1

Comparative Example 2

In a similar manner to Synthesis Example 1, a black-hued electrodeposition coating material (Y-8) composed of 750.0 g of the acrylic resin, 250.0 g of the melamine resin, 61.8 g of triethylamine, 30.0 g of Phthalocyanine Blue, 50.0 g of Phthalocyanine Green and 50.0 g of azo metal salt red pigment was prepared. Using this coating material, a glass substrate having a black-hued coating film having a film thickness of 2 μm was prepared in a manner similar to Example 1. The surface resistivity and the volume resistivity of the coating film were measured and found to be 5×10^{14} ohm/□ and 2×10^{13} ohm·cm, respectively. Using this glass plate, a color filter was prepared in a manner similar to Application Example 1. The optical density of the light-shielding layer of this color filter was 1.10. With this optical density, the color filter could not be practically employed because its characteristics, such as contrast, was extremely low.

Comparative Example 3

In a similar manner to Synthesis Example 2, a black-hued coating material for electrodeposition (Y-9), composed of 750.0 g of the acrylic resin, 250.0 g of the melamine resin, 61.8 g of triethylamine and 1,000 g of nickel was prepared. Using this coating material, a glass substrate having a black-hued coating film having a film thickness of 2 μm was prepared in a manner similar to Example 1. The surface resistivity and the volume resistivity of the coating film were measured and found to be 50 ohm/□ and 40 ohm·cm, respectively. Using this glass substrate, a TFT liquid crystal display device for black and white display was prepared.

The display device had the light-shielding layer of extremely low accuracy because of its poor adhesivity.

Although the present invention has been described with reference to the preferred examples, it should be understood that various modifications and variations can be easily made by those skilled in the art without departing from the spirit of the invention. Accordingly, the foregoing disclosure should be interpreted as illustrative only and is not to be interpreted in a limiting sense. The present invention is limited only by the scope of the following claims.

What is claimed is:

1. A method for preparing a substrate having a light-shielding layer for use as a counterelectrode substrate for a thin film transistor array substrate for black and white display, said method comprising the steps of:
 - i) forming a positive photosensitive coating film on a transparent electrically conductive layer formed on a transparent substrate,
 - ii) exposing said positive photosensitive coating film via a mask exhibiting light transmitting properties only at portions thereof registering with the light-shielding layer,
 - iii) removing and developing the portions of the coating film exposed to light for exposing the transparent electrically conductive layer and electrodepositing a dark-hued coating on at least a portion of the exposed transparent electrically conductive layer for forming the light shielding layer, and
 - iv) heating said light-shielding layer, said light-shielding layer having a volume resistivity of 1×10^2 to 1×10^6 ohm·cm.
2. A method for preparing a substrate having a light-shielding layer for use as a counterelectrode substrate for a thin film transistor array substrate for black and white display, said method comprising the steps of:
 - i) forming a negative photosensitive coating film on a transparent electrically conductive layer formed on a transparent substrate,
 - ii) exposing said negative photosensitive coating film via a mask exhibiting light transmitting properties only at portions thereof other than those registering with the light-shielding layer,
 - iii) removing and developing the portions of the coating film not exposed to light for exposing the transparent electrically conductive layer and electrodepositing a dark-hued coating on at least the exposed transparent electrically conductive layer for forming the light shielding layer, and
 - iv) heating said light-shielding layer, said light-shielding layer having a volume resistivity of 1×10^2 to 1×10^6 ohm·cm.
3. A method for preparing a substrate having a light-shielding layer for a color filter of a liquid crystal display device comprising the steps of:
 - i) forming a positive photosensitive coating film on a transparent electrically conductive layer formed on a transparent substrate,
 - ii) exposing said positive photosensitive coating film via a mask exhibiting light transmitting properties only at portions thereof registering with the light-shielding layer,
 - iii) removing and developing the portions of the coating film exposed to light for exposing the transparent electrically conductive layer and electrodepositing a dark-hued coating on at least a portion of the exposed

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- transparent electrically conductive layer for forming the light shielding layer, and
- iv) heating said light-shielding layer, said light-shielding layer having a volume resistivity of 1×10^6 to 1×10^{12} ohm·cm.
4. A method for preparing a substrate having a light-shielding layer for a color filter of a liquid crystal display device comprising the steps of:
- forming a negative photosensitive coating film on a transparent electrically conductive layer formed on a transparent substrate,
 - exposing said negative photosensitive coating film via a mask exhibiting light transmitting properties only at portions thereof other than those registering with the light-shielding layer,
 - removing and developing the portions of the coating film not exposed to light for exposing the transparent electrically conductive layer and electrodepositing a dark-hued coating on at least the exposed transparent electrically conductive layer for forming the light shielding layer, and
 - heating said light-shielding layer, said light-shielding layer having a volume resistivity of 1×10^6 to 1×10^{12} ohm·cm.

5. The method as claimed in claim 1 or 3 wherein said transparent substrate is selected from the group consisting of quartz, glasses, polyester, polyphenylene sulfide, epoxy resin, acrylic resin, polymethylpentene, polyimides, polycarbonates, polyamides, polysulfones, polyether, polystyrene, acrylonitrile-styrene copolymers, cellulose triacetate and mixtures thereof.

6. The method as claimed in claim 1 or 3 wherein said transparent electrically conductive layer is formed of a material selected from the group consisting of tin oxide, indium oxide, indium-tin oxide and antimony oxide.

7. The method as claimed in claim 1 or 3 wherein said positive coating film is selected from the group consisting of compounds containing quinone diazido groups, compounds having diazomeldrum's acid, compounds having nitrobenzyl esters and a composition containing at least one of said compounds.

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8. The method as claimed in claim 2 or 4 wherein said negative photosensitive coating film contains a material selected from the group consisting of a resin and a prepolymer each having an ethylenic double bond capable of cross-linking by light, a coloring agent selected from the group consisting of a dye, a pigment and mixtures thereof, and a photopolymerization initiator.
9. The method as claimed in claim 2 or 4 wherein said negative photosensitive coating film further contains a low molecular (meth)acrylate.
10. The method as claimed in claim 8 wherein said photopolymerization initiator is selected from the group consisting of benzoins, benzoin ethers, benzyl alkyl ketals, benzophenones, anthraquinones, thioxanthones and mixtures thereof.
11. The method as claimed in claim 1 or 3 wherein said dark-hued coating contains a coloring agent selected from the group consisting of carbon black, graphite, vanadium trioxide, manganese dioxide, molybdenum disulfide, triiron tetroxide, Aniline Black, Sudan Black B, Acid Black 1 and 52, Fast Black K Salt, Nigrosin and mixtures thereof.
12. The method as claimed in claim 2 or 4 wherein said transparent substrate is selected from the group consisting of quartz, glasses, polyester, polyphenylene sulfide, epoxy resin, acrylic resin, polymethylpentene, polyimides, polycarbonates, polyamides, polysulfones, polyether, polystyrene, acrylonitrile styrene copolymers, cellulose triacetate and mixtures thereof.
13. The method as claimed in claim 2 or 4 wherein said transparent electrically conductive layer is formed of a material selected from the group consisting of tin oxide, indium oxide, indium-tin oxide and antimony oxide.
14. The method as claimed in claim 2 or 4 wherein said dark-hued coating contains a coloring agent selected from the group consisting of carbon black, graphite, vanadium trioxide, manganese dioxide, molybdenum disulfide, triiron tetroxides Aniline Black, Sudan Black B, Acid Black 1 and 52, Fast Black K Salt, Nigrosin and mixtures thereof.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,527,649
DATED : June 18, 1996
INVENTOR(S) : Haruyoshi Sato, et. al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page, item [73], Assignee: should read -- Nippon Oil Co.,
Dai Nippon Printing Co., Ltd., both of Tokyo, Japan--

Signed and Sealed this

Fifth Day of November, 1996

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : **5,527,649**
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**Title page, Item [73], Assignee: should read
--Nippon Oil Co., Ltd., and Dai Nippon Printing Co.,
Ltd., both of Tokyo, Japan--.**

This certificate supersedes Certificate of Correction issued November 5, 1996.

Signed and Sealed this
Seventeenth Day of June, 1997

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks



US005998090A

United States Patent [19]

Sabnis et al.

[11] Patent Number: **5,998,090**[45] Date of Patent: **Dec. 7, 1999****[54] HIGH OPTICAL DENSITY ULTRA THIN ORGANIC BLACK MATRIX SYSTEM****[75] Inventors:** Ram W. Sabnis; Terry L. Brewer; Robert E. Nichols; Edith G. Hays, all of Rolla; Michael D. Stroder, Springfield, all of Mo.; Akira Yanagimoto, Musashino, Japan; Yasuhisa Sone, Funabashi, Japan; Yoshitane Watanabe, Tokyo, Japan; Kiyomi Ema, Chiba, Japan**[73] Assignees:** Brewer Science, Inc., Rolla, Mo.; Nissan Chemical Industries, Ltd., Japan**[21] Appl. No.:** 08/982,233**[22] Filed:** Dec. 1, 1997**[51] Int. Cl.⁶** G03F 7/004; C08K 3/04**[52] U.S. Cl.** 430/270.1; 430/7; 524/495; 524/496; 523/215**[58] Field of Search** 430/7, 627, 270.1; 523/215; 524/495, 496**[56] References Cited****U.S. PATENT DOCUMENTS**

4,822,718 4/1989 Latham et al. .

5,176,971 1/1993 Shimamura et al. .
5,368,976 11/1994 Tajima et al. .
5,378,274 1/1995 Yokoyama et al. .
5,587,818 12/1996 Lee .**OTHER PUBLICATIONS**

Asia Display 98, pp. 653-656 by T. Terashita, et al entitled "Fully Self-Aligned Organic Electroluminescent Devices with Dual Side-Wall Structures".

Yamanaka et al., SID Digest—Integrated Black Matrix on TFT Arrays, 1992, 23:789.

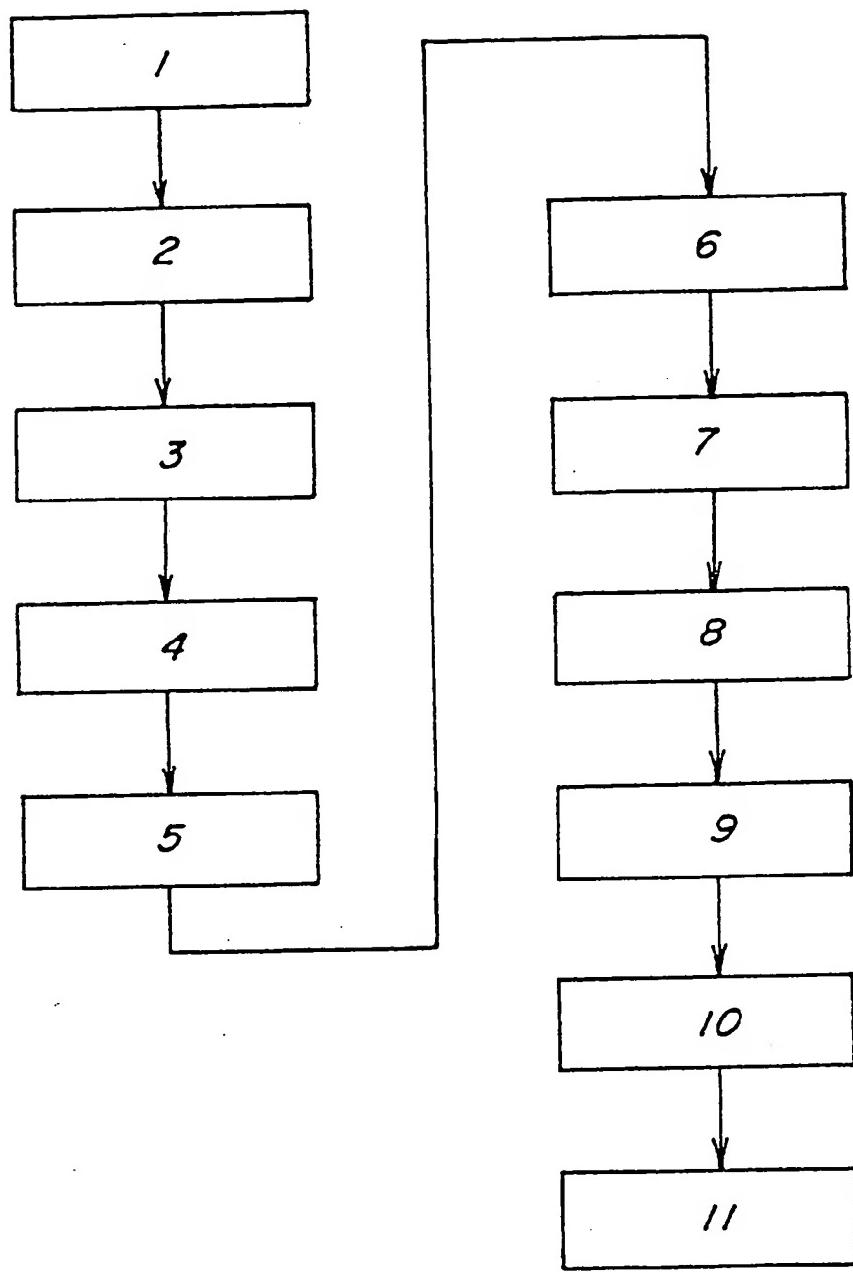
Hesler et al., SID Digest—Pigment-Dispersed Organic Black-Matrix Photoresists for LCD Color Filters, 1995, 26:446.

Hasumi et al., EURO Display 96—Carbon Dispersed Organic Black Matrix on Thin Film Transistor Liquid Crystal Display, 1996, 16:237.

Primary Examiner—Tae Yoon*Attorney, Agent, or Firm*—Veo Peoples, Jr.; Holly M. Amjad**[57] ABSTRACT**

A high optical density, i.e., ≥ 3.0 , at 1 micron or less film thickness, black matrix is disclosed having improved stability and shelf life as a consequence of admixing Pigment Black 7 and organic dye or dye mixtures on a polyimide polymer vehicle.

11 Claims, 8 Drawing Sheets



FLOW CHART OF MANUFACTURING
PROCESS OF BM

Fig. 1

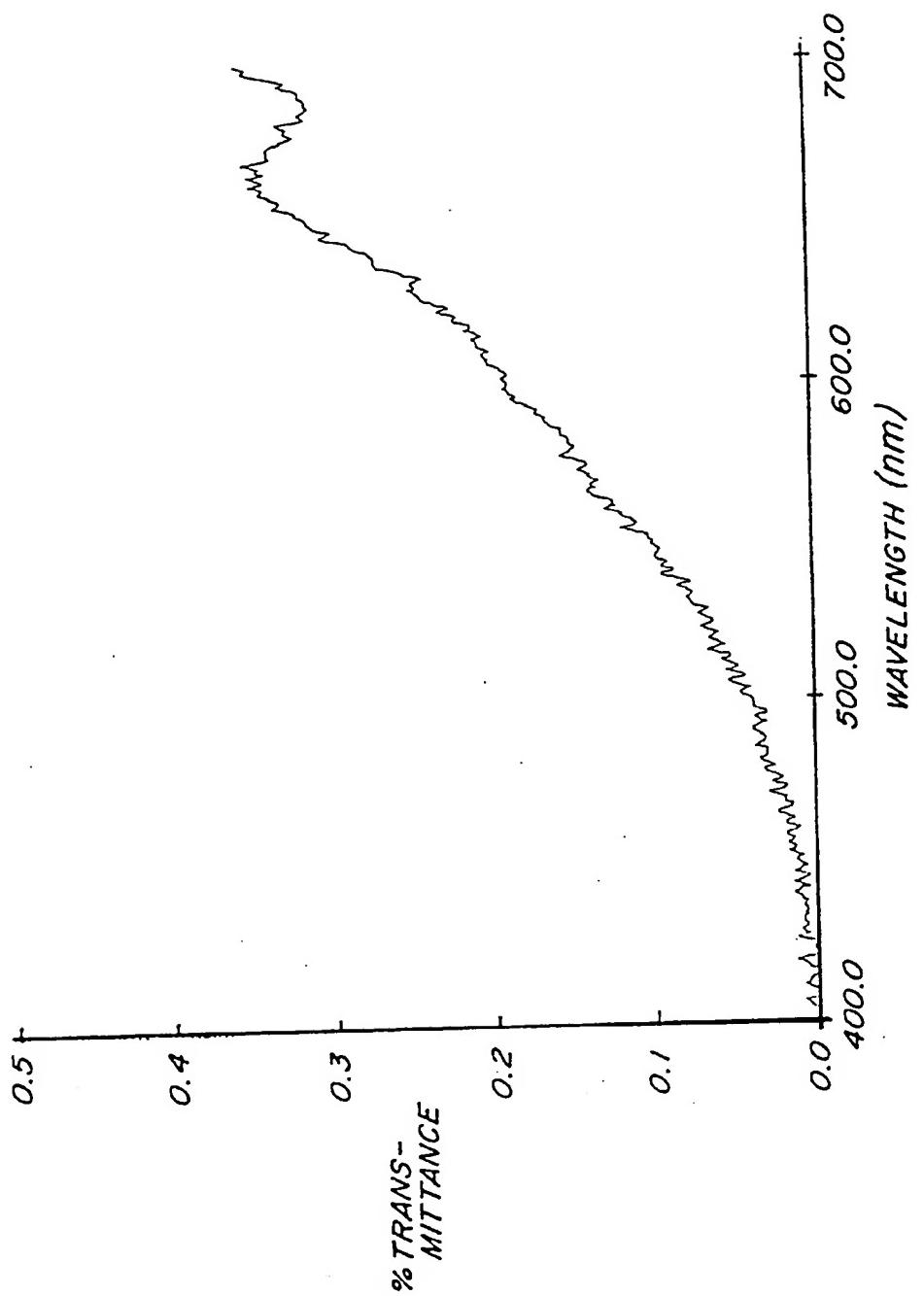


Fig. 2

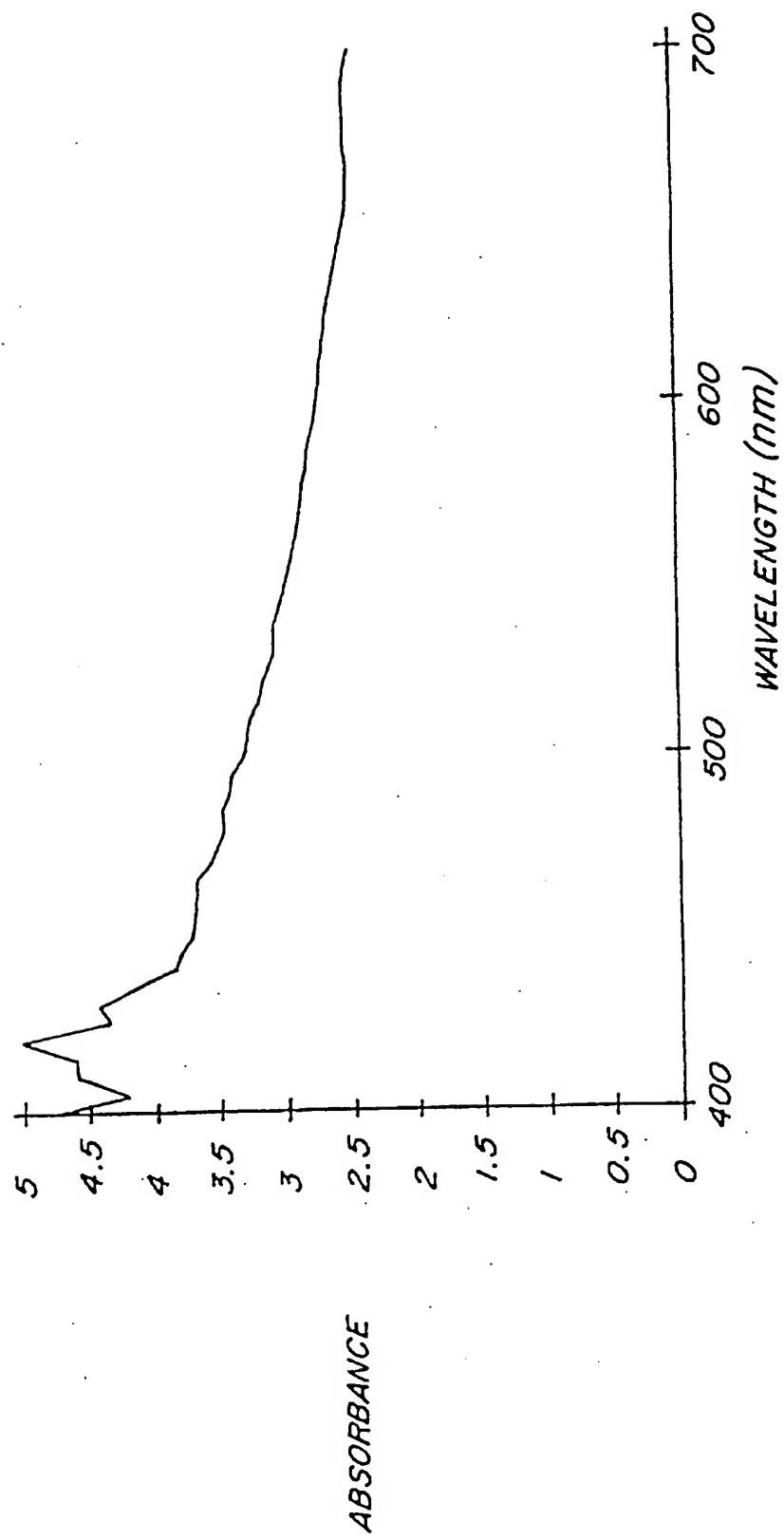


Fig. 3

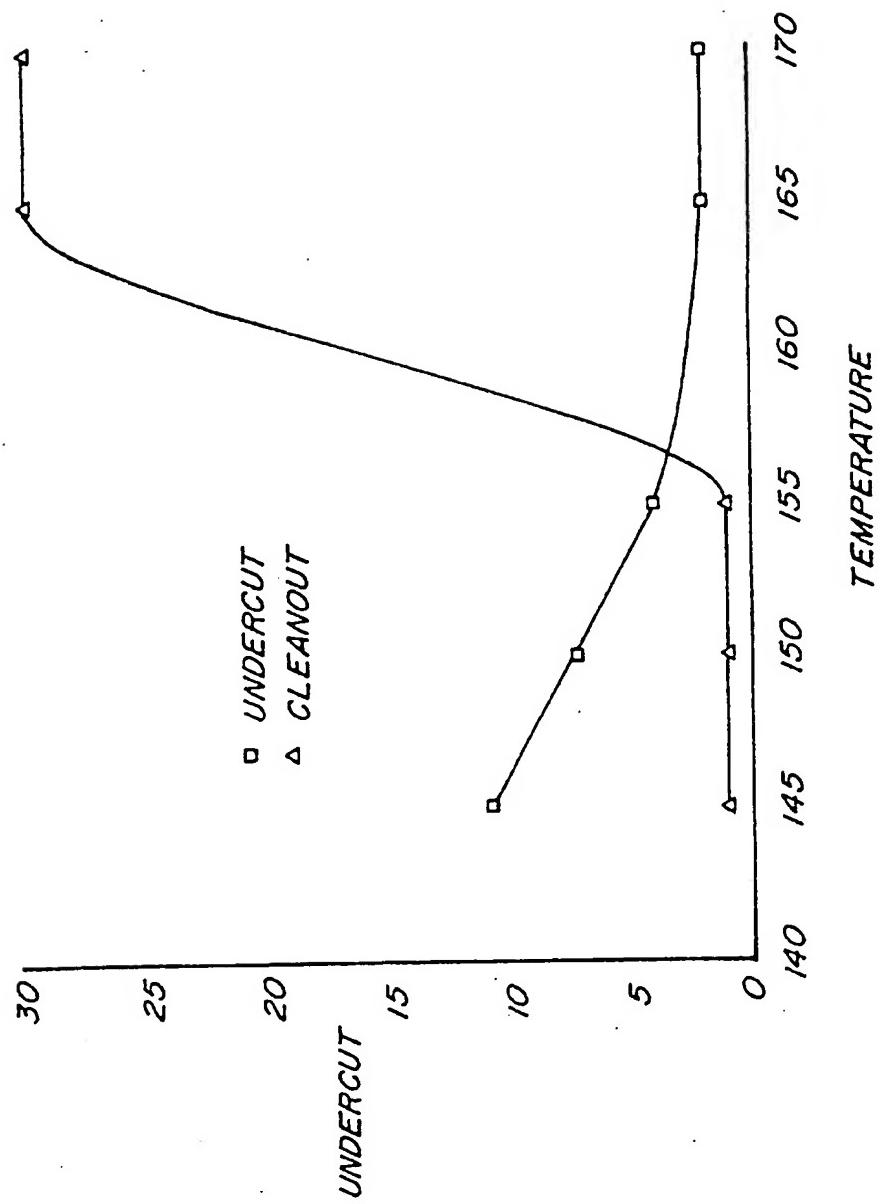


Fig. 4

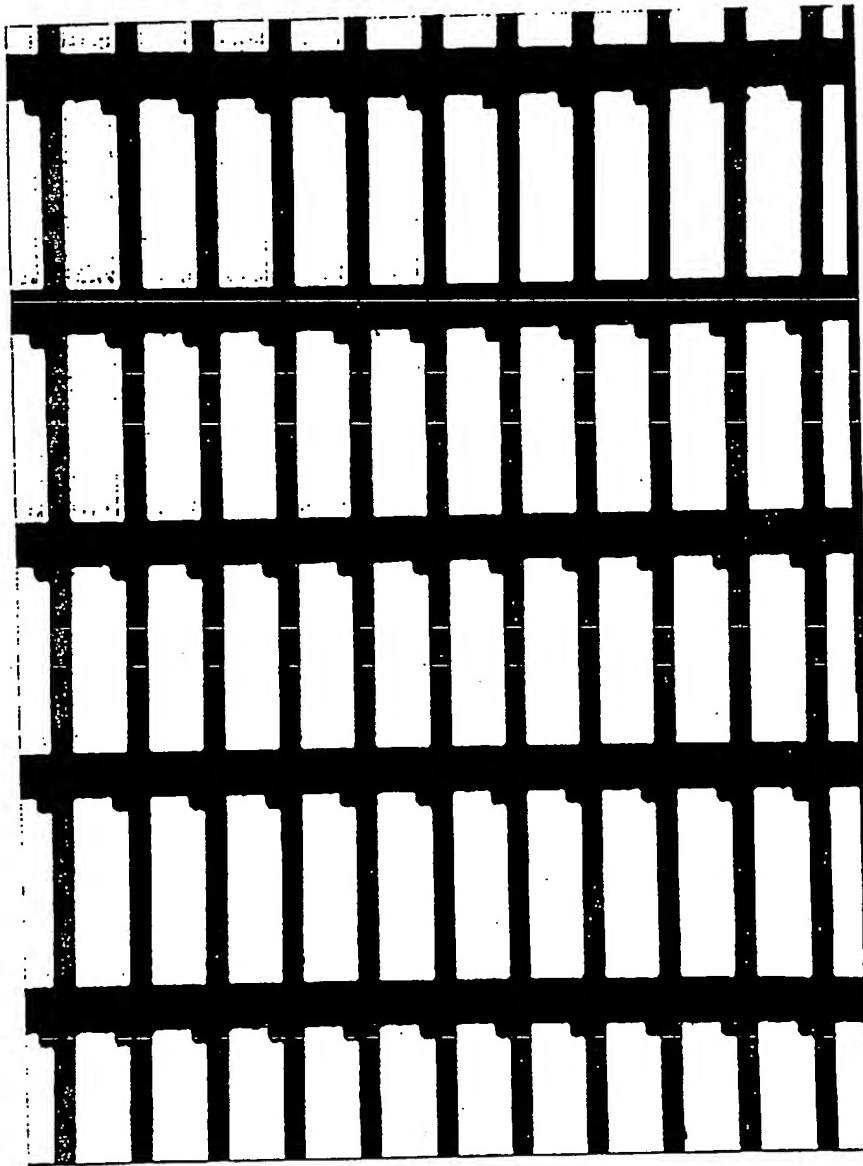


Fig. 5

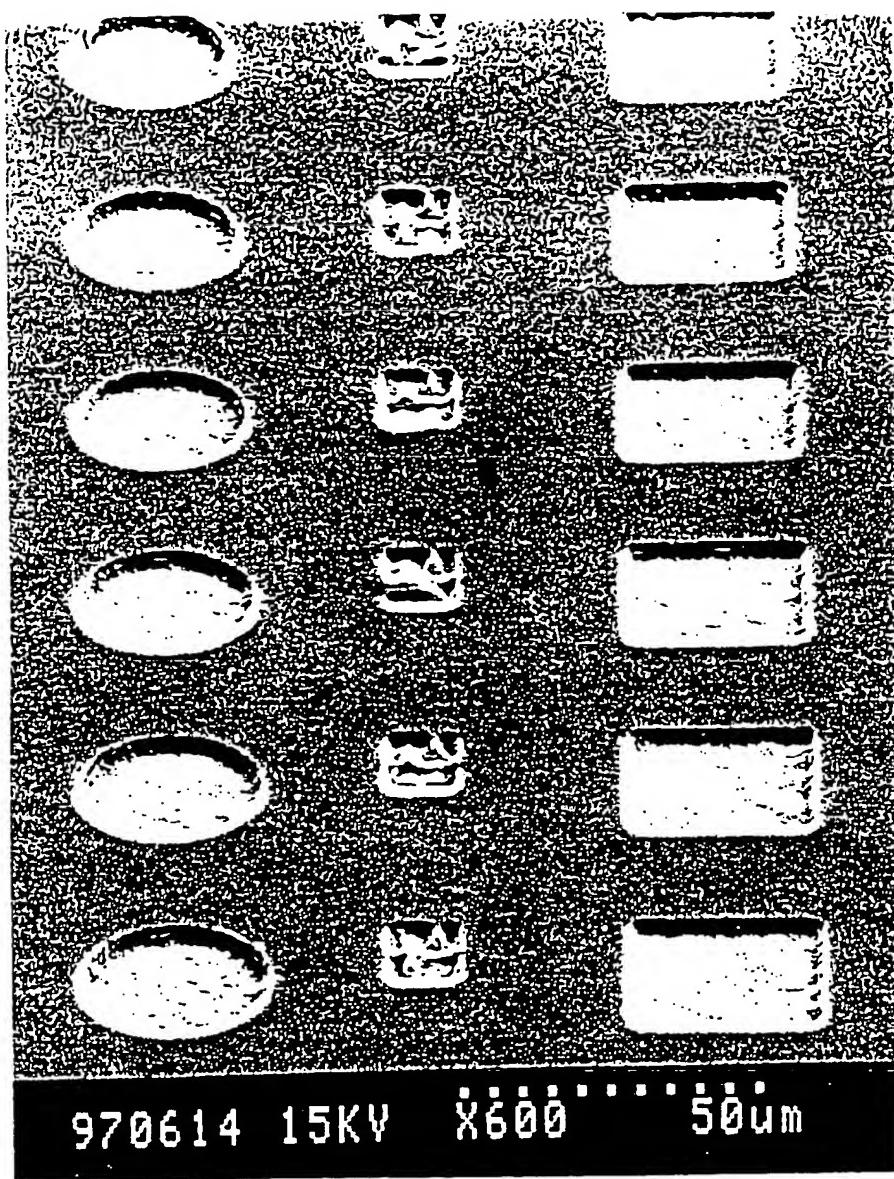


Fig. 6

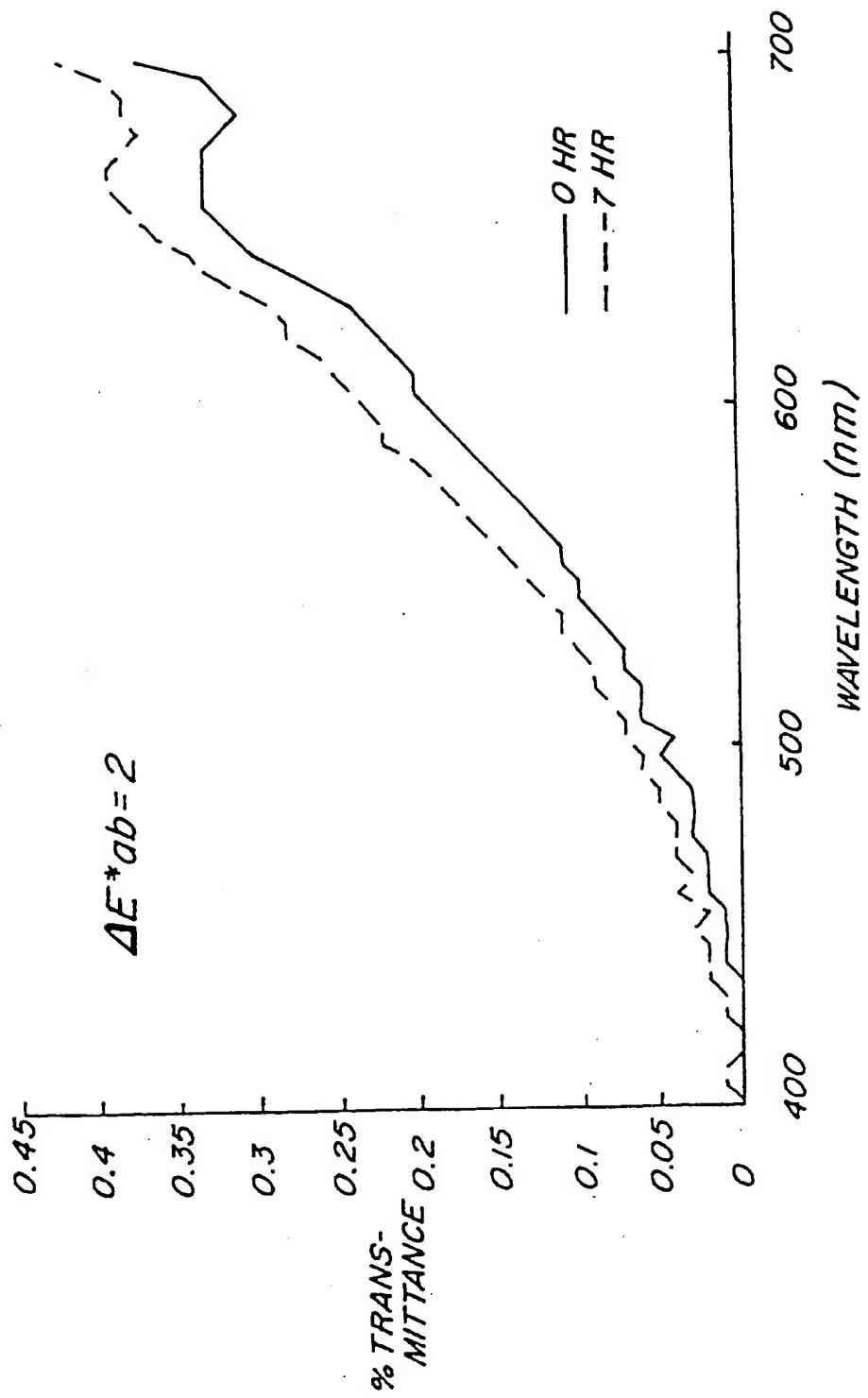


Fig. 7

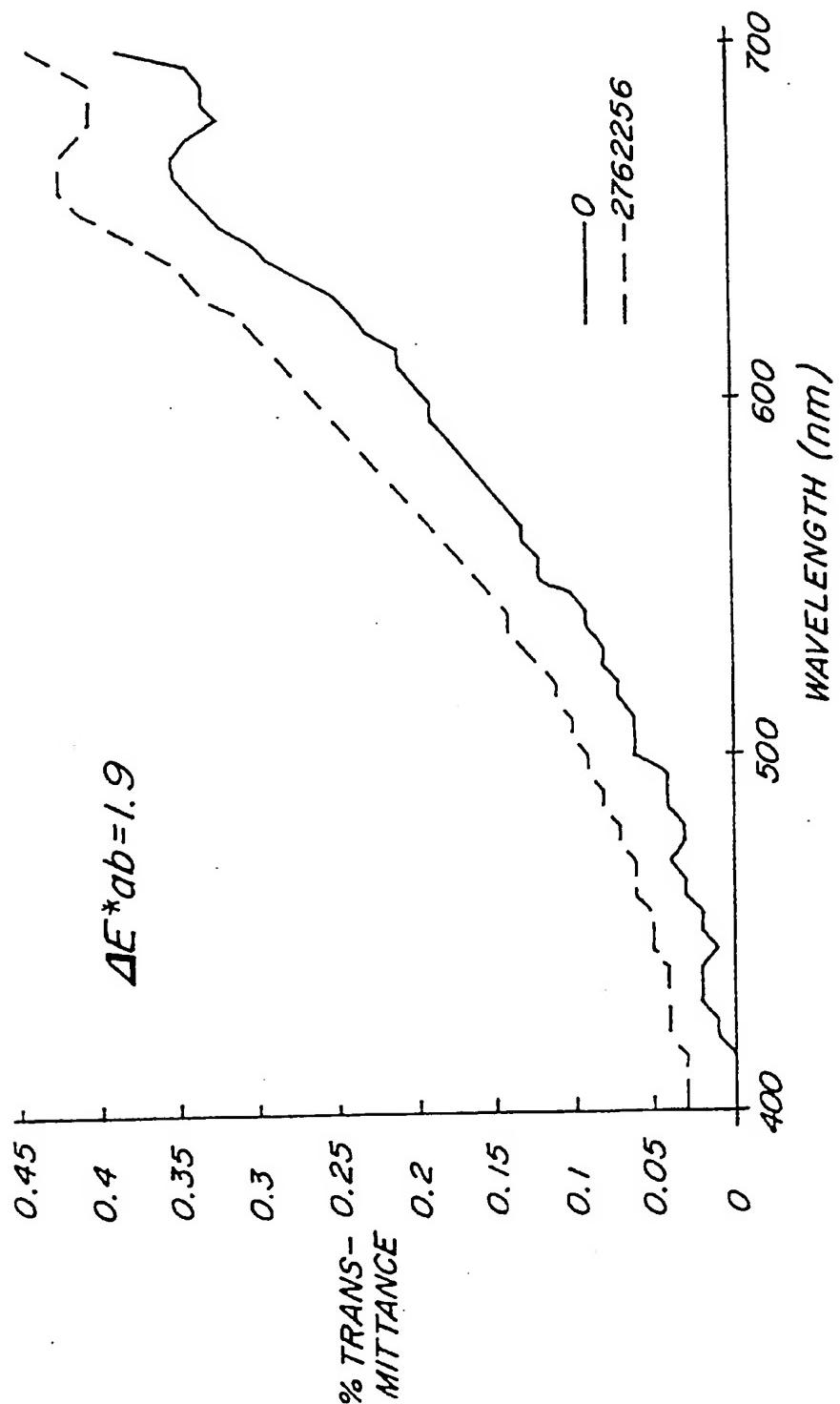


Fig. 8

HIGH OPTICAL DENSITY ULTRA THIN ORGANIC BLACK MATRIX SYSTEM

BACKGROUND OF INVENTION

1. Field of Invention

The present invention relates to organic black matrices for color filter plate manufacture and to methods for making the same. It particularly relates to black matrices, having high optical density at ultra thin film thicknesses, excellent evenness, high strength, low cost and being useful for the production of a variety of display devices.

2. Background of the Prior Art

Multicolor liquid crystal displays (LCDs) are routinely produced having a thin, light-absorbent film, called a black matrix, applied to an array of color pixels which together form a color filter plate. The processing of such color filter plates remains one of the most troublesome steps during mass production of the LCDs because such processing normally employs a black matrix film made from sputtered chrome.

A spin-coatable, organic polymer based black matrix would tend to be more environmentally friendly than chrome, easier to reproduce, and offer lithographic processing advantages. However, there are at least two types of color filter plates for LCDs where organic polymer black matrices are woefully expensive and/or lack the desired performance. That is, the unavailability of an organic black matrix photoresist having sufficiently high optical density at ultra thin film thickness, has hampered the advancement of 1) thin film transistor (TFT)-arrays for TFT-LCDs and 2) super twisted nematic (STN) LCDs.

The optical density (O.D.) of the black matrix must be greater than 2.0 in order to block the transmission of light to the TFT or STN displays. Otherwise, photo leaks from non-display areas will reduce the contrast ratio and create adverse photo leakage current. In other words, one can enhance the contrast of the LCD by eliminating the light leakage which would otherwise occur through spaces patterned between the red, green, and blue (RGB) pixels on the color filter plate. The technical goal is to keep the light transmission at or below 1%, across the entire spectrum of from ultraviolet to infrared, at ultra thin black matrix film thicknesses.

It has proven extremely difficult, if not impossible, to manufacture an organic black matrix having an O.D. of ≥ 3.0 at ultra thin black matrix film thicknesses. Although O.D. greater than, or equal to, 2.0 have been achieved for organic black matrices at a 2 micron polymer thickness, such thick layers tend to cause a number of defects. For example, the so-called reverse tilt inside each pixel display area occurs at a gap of 2 microns. Reverse tilt causes defects in image and contrast deterioration. Overcoming that drawback, inter alia, requires an organic black matrix film having O.D. greater than 2.0 at a thickness of 1.0 micron or less.

Chrome Based Black Matrix

Therefore, despite

- 1) the high cost-of-ownership,
- 2) the complexity of the sputtering process,
- 3) the potential environmental problems, and
- 4) a higher reflectance than desired,

the most common black matrix material has continued to be sputtered chrome. Vacuum evaporation and other coating techniques for metals such as nickel, aluminum and even

chromium have been contemplated, but sputtering remains the most common technique and chrome remains the most common material, because other techniques and other materials, thus far, lack sufficiently high O.D. (≥ 3.0) to provide enhanced contrast and high resolution, at sufficiently ultra thin thicknesses (1 micron or less) to be commercially effective for various display applications such as TFT and STN.

U.S. Pat. No. 5,378,274 by Yokoyama, et al., and U.S. Pat. No. 5,587,818 by S. Lee disclose typical chrome based black matrices for LCD's. That is, chromium is sputtered to form a thin film of about 2000 Å. As previously discussed, such sputtering is an undesirably complex and expensive manufacturing process which poses serious environmental problems.

15 Dye Based Black Matrix Systems

U.S. Pat. No. 4,822,718 by Latham discloses an alternative potential black matrix for color filters. It contains a polyimide precursor vehicle and dyes. The color filters are used in color liquid crystal displays, light emitting diodes, photodiodes, and solid state lasers. However these black matrix compositions have several drawbacks, as a consequence of using dyes, rather than pigments, as the coloring agents. The dyed systems have lower heat, light and chemical resistance than desired for many applications. Moreover, dyes are not completely soluble in the solvent and polyimide vehicle system, thus the dyes fail to absorb light across a sufficiently broad spectrum of wavelengths. For example, Latham uses blue and brown dyes and, while not illustrating any data on optical density, we have that the desired optical density (≥ 3.0) is not achievable using blue and brown dyes. Also, the dyed composition has long process steps which tend to lower production yield and raise fabrication cost.

U.S. Pat. No. 5,176,971 by Shimamura, et al., also discloses a dyed black matrix composition for color filters, which contains dyes and a polyimide precursor vehicle for use in color LCD devices. Its system is subject to fading as a consequence of the composition's limited heat stability. The dyes are said to have a relatively low thermal resistance. Additionally, a resin-surface modifier is added to the composition so as to impart water and oil repellency to the surface of the coating layer. The presence of excessive amounts of this surface modifier, however, impedes control of the uniformity of the thickness of the coating layer. Thus, even with the surface modifiers, the composition shows poor performance with respect to heat, light and chemical fastness. Furthermore, relative weight proportions of dye and polyimide must be carefully controlled; otherwise excessive dye will leak into the photoresist at a later step.

50 Pigment-Carbon Black Based Black Matrix Systems

It has been disclosed by Hesler, et al., in the article "Pigment-Dispersed Organic Black Matrix Photoresists for LCD Color Filters," *SID Digest*, 26:446 (1995); that carbon black dispersed in acrylic polymer provided an average optical density of 2.8 for 1.5 μm film thickness. However it reports poor reproducibility and poor coating properties. The composition needed improvement in image quality.

As disclosed by Yamanaka, et al., in his article, "Integrated Black Matrix on TFT Arrays," *SID Digest*, 23:789 (1992); carbon black, even with advanced acrylic photo polymer, does not achieve OD greater than 2.0, at thickness less than 2 μm without creating crosstalk. Yamanaka also describes the disadvantage of a 2 μm "step size" (or thickness). It is so large that it results in reverse tilt inside each pixel display area. This causes spot defects in image and contrast deterioration.

Hasumi, et al., in his article "Carbon Dispersed Organic Black Matrix on Thin Film Transistor," *Proc. of Int. Display*

Res. Conf. (EuroDisplay-96), 16:237 (1996) also discloses a carbon black dispersed system providing OD more than 2.0 at 1.5 μm film thickness, but presumably, like Yamanaka, it is also subject to crosstalk.

U.S. Pat. No. 5,368,976 by Tajima, et al., discloses another pigment-dispersed color filter composition useful for the production of LCD and charged coupled devices. The system requires controlling the molecular weight (M.W.) of a radiation-sensitive acrylic block copolymer vehicle. If M.W. exceeds 500,000, then scum develops around the pixels, causing insufficient sharpness at pattern edge, surface soiling, and excess resin at non-pixel portions. If M.W. is less than 10,000, the development time margin is deleteriously decreased. The radiation-sensitive copolymer composition promotes adhesion to the substrate, facilitates transmittance and aids in color contrast. The acrylic type copolymer has limited thermal stability and poor photo-speed. The pigment, copolymer and a radiation sensitive component are dispersed via grinding in a ball mill for 18 hours which is unduly time consuming. The dispersed pigment is filtered through a 10 μm filter which allows pigment particle sizes in the formulation which fabricate into low transparency film. The shelf life of one week in a dark place at room temperature is too short. The dispersion needs dark conditions and is not stable after one week. The composition uses Pigment Black 1 and Pigment Black 7 only. Pigment Black 1 does not provide high optical density and the process does not use any dyes.

In summary, the previous black matrices have several drawbacks which may be listed as follows:

Chrome based black matrix suffers from, *inter alia*, high cost, poor adhesion, and toxicity concerns.

Dyed matrices are limited by the generally lower absorptivity of black dyes in comparison to black pigments and the limited solubility of such dyes either in solvents or a polymer matrix. Also, dyed formulations do not provide sufficient heat, light and chemical stability.

Pigmented coatings suffer from one or more of the following problems: 1) the formulations are unstable against gelation or flocculation at the required high carbon black loadings, making it very difficult to have long shelf life for the pigmented systems; 2) if the formulations are designed to be photosensitive, they can not be too highly loaded with carbon black without losing their imaging properties; and 3) formulations containing non-carbon black pigments do not provide very high optical density, while 4) carbon black pigments have particle sizes too large to permit sufficiently thin layer thickness at the requisite high optical densities.

The cited prior art reveals the need for a black matrix composition with very high optical density (≥ 3.0), and with heat, light, and chemical fastness and longer shelf life. The prior art also illustrates the need for a composition with low cost, less manufacturing (and processing) time, long shelf life, and environmentally safe.

SUMMARY OF THE INVENTION

The present invention is directed towards a black matrix composition comprising a pigment:dye system for use in the manufacture of various display applications. This black matrix: 1) can be applied by spin coating; 2) can be imaged using the same process used for RGB pixels; 3) can be developed using the same process used for RGB pixels; 4) the average optical density for the 1 μm or less film thicknesses over the region 400–700 nm of ≥ 3.0 (very high); 5) has longer shelf life (can be more than three months at room temperature and more than one year in freezer); 6) less grinding time; 7) less spin coat time; 8) inexpensive

pigments; 9) excellent coating and imaging characteristics; and (10) much lower manufacturing cost compared to chrome black matrices.

The composition keeps transmission at or below 1% across the spectrum at a film thickness of 1 μm or less (ensuring O.D. ≥ 3.0), while achieving excellent imaging characteristics. This system is a high performance, low cost alternative to chrome.

The inventors have developed a novel very high optical density ($\geq 3.0 @ 1 \mu\text{m}$ or less film thicknesses) black matrix system for a wide variety of display applications including, for example, TFT, TN, STN, EL, and plasma.

It is therefore a principle object of the present invention to provide a superior black matrix system.

It is a further object of the present invention to provide a novel method and composition having high heat, light, chemical resistance and high adhesive strength, particularly on glass substrates.

It is an additional principle objective of the invention to provide a very high optical density material well suited for various display applications and which can be applied by spin coating and patterned by photolithography.

It is also an object of the invention to provide a simpler process with higher performance standards and superior environmental safety.

It is an additional object of the invention to provide a system with high yield, less manufacturing and processing time, and excellent shelf life at low cost compared to chrome black matrices.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow chart explaining the manufacturing process of a black matrix according to the present invention.

FIG. 2 is a graph showing transmission spectra of 1 μm cured film obtained in Example 1.

FIG. 3 is a graph showing absorbance spectra of 1 μm cured film obtained in Example 1 (optical density=absorbance @ 540 nm)

FIG. 4 shows sets of lithography data using both convection oven and hot-plate β -bake processes.

FIG. 5 is a schematic diagram illustrating photo of a resolution dagger.

FIG. 6 demonstrates Scanning Electron Microscope (SEM) of the black matrix material after resist removal and final cure.

FIG. 7 demonstrates excellent thermal stability at 230° C. for 7 hours for Example 1.

FIG. 8 demonstrates the superior light resistance of the black matrix from Example 1 after 2.8 million lux hours exposure.

DETAILED DESCRIPTION OF THE INVENTION

The role of black matrix is to block the TFT from light and to protect the contrast ratio from reduction which might arise from possible photoleaks through nondisplay areas.

The novel black matrix system of the present invention is characterized by an optical density of equal to or greater than 3.0 at a cured film thickness of 1 μm or less. The system comprises a pigment:dye combination in a predetermined proportion. The polymer vehicle for the black matrix of the present invention typically includes a polyimide precursor which reacts in situ to form a polyimide resin. The pigment

component of the composition is an inexpensive, high performance carbon black, preferably Pigment Black 7. The dye component may be a solvent soluble, light absorbing dye, preferably a blue and brown mixture. Suitable solvents include cyclic ketones, alcohols, esters, ethers and their mixtures. The pigment and dyes used in the present invention are preferably compatible with the polyimide resin and a suitable dispersant.

Typical Compositions

Polyimides are well known for high thermal stability, resistivity and dielectric strength. They provide excellent imaging characteristics, dyeability and coating properties. The vehicle for black matrix typically includes a polyimide precursor which reacts in use to form a polyimide resin. The precursor typically includes a polyamic acid (PAA) prepared by reacting oxydianiline (ODA) with pyromellitic dianhydride (PMDA) and/or benzophenone tetracarboxylic dianhydride (BTDA). The vehicle components being present in appropriate stoichiometric amounts (U.S. Pat. No. 4,822,718). Other equivalent polyamic acids and polyamic precursors may be used which are summarized in Table 1.

TABLE 1

DIAMINES	DIANHYDRIDES
p-Phenylenediamine	3,3',4,4'-Benzophenone-tetracarboxylic dianhydride
3,3'-dimethyl-4,4'-diaminobiphenyl	Pyromellitic dianhydride
1,4-bis(4-aminophenoxy)benzene	3,3',4,4'-Biphenyl tetracarboxylic dianhydride
4,4'-Bis(4-aminophenoxy)-biphenyl	4,4'-Oxydiphtalic anhydride
Bis-4-(4-aminophenoxy)phenyl ether	3,3',4,4'-Diphenylsulfone tetracarboxylic-dianhydride
4,4'-Oxydianiline	1,2,3,4-cyclobutane-tetracarboxylic dianhydride
4,4'-Diaminodiphenyl sulfide	
4,4'-Diaminodiphenyl sulfone	
2,2'-Bis[4-(4-aminophenoxy)phenyl]sulfone	
9,10-bis(4-aminophenyl)-anthracene	

mance and low cost carbon black pigments which are preferred for the very high optical density required in TFT, TN, STN, EL and plasma applications include the different types and grades of high color, low cost, surface treated carbon black pigments which are listed in the Color Index as Pigment Black 7, C.I. #77266. The final particle size of the pigment is 0.01 to 0.2 microns. Pigment Black 7 may be known as acetylene black, channel black, furnace black, and thermal black. Examples of tradenames for Pigment Black 7 are parenthetically expressed as set forth below. Pigment Black 7 (Monarch 1000; Cabot Corporation), Pigment Black 7 (Monarch 1100; Cabot Corporation), Pigment Black 7 (Monarch 1300; Cabot Corporation), Pigment Black 7 (Monarch 1400; Cabot Corporation), Pigment Black 7 (Raven 7000; Columbian Chemical Co.), Pigment Black 7 (Raven 5000 Ultra; Columbian Chemical Co.), Pigment Black 7 (Special Black FW 200; Degussa Corporation), Pigment Black 7 (Special Black 6; Degussa Corporation), Pigment Black 7 (Special Black 4; Degussa Corporation).

Examples of solvent soluble, light absorbing dyes useful in the present invention are DARC 100 (Brewer Science, Inc.; U.S. Pat. No. 5,340,619), Solvent Black 35 (Zapon Black X50; BASF Corporation), Solvent Black 27 (Zapon Black X51; BASF Corporation), Solvent Black 3 (Neptun Black X60; BASF Corporation), Solvent Black 5 (Flexo Black X12; BASF Corporation), Solvent Black 7 (Neptun Black NB X14; BASF Corporation), Solvent Black 46 (Neptun A Black X17; BASF Corporation), Solvent Black 47 (Neopen Black X58; BASF Corporation), Solvent Black 28 (Orasol Black CN; Ciba-Geigy Corporation), Solvent Black 29 (Orasol Black RL; Ciba-Geigy Corporation), Solvent Black 45 (Saviny Black RLS; Sandoz Corporation).

Table 2 shows examples of compositions of the invention evaluated along with their effects on the shelf life of the black matrix. Polyimides in Table 2 are polyamic acids typically prepared by reacting ODA with PMDA and/or BTDA. The dyes used in DARC 100 are typically a mixture of Solvent Brown 44 (Orasol brown LRL) and Solvent Blue 67 (Orasol blue GN), the ratio of which is from 1:3 to 5:1 by weight, preferably 1.3:1.0. Disperbyk 164 is used in each sample and the amount of Pigment Black 7 was the same as in Example 1.

TABLE 2

DYE COMPONENT/	SHELF LIFE OF BLACK MATRIX				
	C. I. NAME	POLYMER	COMPANY	ROOM TEMPERATURE	FREEZER
No dyes	Polyimide	—		1 day	3 days
DARC 100 ®	Polyimide	Brewer Science, Inc.		>90 days	>365 days
Solvent Black 35	Polyimide	BASF Corporation		34 days	90 days
Solvent Black 27	Polyimide	BASF Corporation		5 days	19 days
Solvent Black 3	Polyimide	BASF Corporation		14 days	40 days
Solvent Black 5	Polyimide	BASF Corporation		10 days	36 days
Solvent Black 7	Polyimide	BASF Corporation		12 days	39 days
Solvent Black 46	Polyimide	BASF Corporation		4 days	16 days
Solvent Black 47	Polyimide	BASF Corporation		5 days	18 days
Solvent Black 28	Polyimide	Ciba-Geigy Corporation		13 days	38 days
Solvent Black 29	Polyimide	Ciba-Geigy Corporation		12 days	40 days
Solvent Black 45	Polyimide	Sandoz Corporation		36 days	92 days

Pigments of the present invention are macroscopic particles having high surface area and a strong tendency to flocculate. Flocculation can create haze and light scattering aggregates and cause inconsistent processing as a result of variations in solution rheology. However, in the present invention, a stable dispersion with superior processing and performance characteristics is achieved. Examples of the high perfor-

A broad spectrum of dispersants were screened by measuring the viscosity of pigment dispersion at different shear rates. The viscosity of a Newtonian dispersion is independent of the rate of shear. Table 3 represents the various dispersants evaluated, and includes the stability of the dispersions.

TABLE 3

DISPERSING AGENT	COMPANY	CLASS	STABILITY OF DISPERSION
Disperbyk-160	Byk-Chemie	Cationic	8 hrs.
Disperbyk-161	Byk-Chemie	Cationic	10 hrs.
Disperbyk-162	Byk-Chemie	Cationic	8 hrs.
Disperbyk-163	Byk-Chemie	Cationic	22 hrs.
Disperbyk-164	Byk-Chemie	Cationic	24 hrs.
Disperbyk-166	Byk-Chemie	Cationic	3 hrs.
Lactimon	Byk-Chemie	Anionic	8 hrs.
Bykumen	Byk-Chemie	Anionic	10 hrs.
Dumasperse 535	Hickson	Anionic	2 hrs.
Dumasperse 540	Hickson	Anionic	8 hrs.
Dumasperse 545	Hickson	Anionic	1 hr.
Mazspperse 85B	PPG	Nonionic	10 hrs.
Mazspperse SF 19	PPG	Nonionic	3 hrs.
Nuosperse 657	Huls	Nonionic	2 hrs.
Nuosperse 700	Huls	Anionic	9 hrs.
Solsperse 12000	Zeneca	Anionic	3 hrs.
Solsperse 27000	Zeneca	Nonionic	8 hrs.

Some dispersants are completely ineffective, whereas others give fair results. Suitable dispersants include Disperbyk-163 (BYK-Chemie, USA) and Disperbyk-164 (BYK-Chemie, USA). Disperbyk-163 is a cationic dispersant composed of solution of higher molecular weight blocked copolymers with groups having strong affinity to pigments. It is less polar and is used primarily in general industrial coatings and to produce pigment concentrates. It provides a preferred embodiment and an improvement over others during storage stability tests. It shows good compatibility with resin, pigments and solvents. Disperbyk-164 is a cationic dispersant composed of solution with high molecular weight block copolymers with groups having strong affinity to pigments. It is less polar and its solids content is higher. It does not contain aromatics. It provides even better storage stability than Disperbyk 163. Suitable solvents include N-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAC), dimethylformamide (DMF), cyclohexanone, bis-2-methylethyl ether (diglyme), tetrahydrofurfuryl alcohol (THFA), dimethylsulfoxide (DMSO), xylenes, cyclic ketones, alcohols, esters, ethers and their mixtures.

Particularly Preferred Embodiments and Best Mode

The polymer vehicle for the preferred black matrix of the present invention includes a polyimide precursor which reacts in situ to form a polyimide resin. The precursor typically includes a polyamic acid prepared by reacting oxydianiline (ODA) with pyromellitic dianhydride (PMDA) and/or benzophenone tetracarboxylic dianhydride (BTDA). Other equivalent polyamic acids and polyamic precursors may be used; however, that sold under the trade name DARC polymer by Brewer Science is particularly preferred. Its components are present in appropriate stoichiometric amounts. (See U.S. Pat. No. 4,822,718.) Pigment Black 7 (Monarch 1000; Cabot Corporation) produced particularly preferred results for very high optical density and generating stable dispersions. The combination of brown and blue dyes at a weight:weight ratio of about 1.377:1.0 sold under the name DARC 100 (Brewer Science, Inc.; U.S. Pat. No. 5,340,619) and previously described is particularly preferred because it provides uniform coating and exceptional stability. (See Table 2.) Disperbyk-164 (BYK-Chemie, USA), was surprisingly stable and yielded the best mode dispersant. It improves pigment wetting, reduces the time required for the grinding process, prevents re-flocculation of the pigments, prevents hard sedimentation, reduces viscosity and avoids thixotropy, maintains better flow (rheology), prevents flood-

ing and floating of the pigments, thus improving the degree of dispersion, and increases the gloss and color strength of the finished products. It shows excellent compatibility with resin, pigments and solvents. The most preferred solvents for the composition of the present invention are N-methyl-2-pyrrolidone (NMP) and cyclohexanone, or mixtures thereof.

The following examples illustrate the process and product of the present invention. The pigment dispersion is carried out in Eiger Mini-100 motor mill using 0.65 mm yttrium stabilized zirconium oxide beads. All percentages are by weight unless otherwise stated.

EXAMPLE 1

In a plastic beaker equipped with mechanical stirrer is added 24.06 g of N-methyl-pyrrolidone (NMP), 105.84 g of cyclohexanone, 3.776 g of Disperbyk-164, 41.22 g of DARC polymer solution (22.9% solids in NMP only), 18.88 g of Monarch 1000 pigment and 60 g of DARC 100 dye solution. The mixture is stirred at 3000 rpm for 15 min. This pigment slurry is then added to Eiger M-100 mill at 1000 rpm over a period of 15 minutes. The beaker is then rinsed with 50 g of N-methyl-pyrrolidone and rinse added to the mill. The grind speed is slowly increased to 3000 rpm. The mill is then run at 3000 rpm for 90 minutes. Formulation is then filtered through 0.2 μm filters. The formulation is summarized in Table 4.

TABLE 4

CHEMICAL CONSTITUENT WEIGHT IN GRAMS	
N-methyl-pyrrolidone:	74.06 g
Cyclohexanone:	105.84 g
Disperbyk-164:	3.776 g (20% of the weight of pigment)
DARC polymer polyamic acid solution:	41.22 g (22.9% solids in NMP only)
Monarch 1000 pigment:	18.88 g
DARC 100 dye solution:	60 g

DARC 100 solution typically contains 320 parts dye solids, 400 parts polymer solids and 3,280 parts solvent. Table 5 illustrates general composition with reference to weight %.

TABLE 5

CHEMICAL COMPOSITION	WEIGHT %
Polyamic acid	15%-20%
Colorant	25%-30%
Dispersant	0.8%-1.0%
Solvent	50%-55%

Referring to FIG. 2, a graph is depicted showing transmission spectra of the 1 μm film obtained in Example 1 wherein the goal of high optical density is achieved. FIG. 3 is a graph showing absorbance spectra of the 1 μm cured film obtained in Example 1 (optical density=absorbance @ 540 nm). FIG. 4 shows sets of lithography data using both convection oven and hot-plate β -bake processes. Lithography results show a wide processing latitude. Resolution down to 3 μm at 1 μm film thickness are achievable within a wide range of intermediate (β -bake) temperatures. FIG. 5 is a schematic diagram illustrating photo of a resolution dagger. FIG. 6 demonstrates Scanning Electron Microscope (SEM) of the black matrix material after resist removal and final cure. Good sidewall definition is evident in the pixel patterns.

FIG. 7 represents high thermal stability (at $\geq 230^\circ \text{C}$) obtained in Example 1. Thermal stability: BM must exhibit

high heat resistance for display applications. FIG. 7 shows the spectral change of Example 1 at 1 μm film thickness before and after heating. The chromatic change (ΔE^*_{ab}) is less than 3 ($\Delta E^*_{ab}=2$) after heating in convection oven at 230° C. in air for 7 hours. Thus, the black matrix shows excellent thermal stability.

The light-resistance of the pixels is critical because these pixels are illuminated from the back light of, for example, liquid crystal displays. The black matrix at Example 1 was exposed to a Mercury-Xenon lamp (200–1300 lux) with UV cut filter. FIG. 8 shows the spectral changes of the black matrix in Example 1 after 2.8 million lux hours of exposure. The chromatic changes (ΔE^*_{ab}) upon exposure are less than 3 ($\Delta E^*_{ab}=1.9$), demonstrating the superior light resistance of the black matrix.

Since color filters are exposed to solvents, acids and bases during the liquid crystal display fabrication process, chemical stability is, as earlier stated, an especially improved performance characteristic. Resistance to acids during etching of indium tin oxide (ITO) electrodes to N-methyl-2-pyrrolidone (NMP) or γ -butyrolactone commonly used as solvents for alignment layer materials and to alkalies, alcohols or detergents during cleaning of the color filters is critical. The chemical stability of black resist was evaluated by both pattern observation and chromatic changes. After dipping the pixels in the above mentioned chemical solutions for 30 minutes, patterns were found to be stable and neither swelling nor peeling was observed. (See Table 6.) The chromatic changes (ΔE^*_{ab}) are less than 1, indicating very good chemical stability of the black matrix.

TABLE 6

CHEMICALS	CHROMATIC CHANGES (ΔE^*_{ab}) AFTER DIPPING FOR 30 MINUTES	
N-methyl-2-pyrrolidone	0.11	
Ethanol	0.44	
Acetone	0.50	
γ -Butyrolactone	0.45	
Isopropyl alcohol	0.81	
Cyclohexanone	0.23	
Propylene glycol monomethyl ether acetate	0.61	
5% Hydrochloric acid	0.38	
5% Sodium carbonate	0.85	
5% Tetramethyl ammonium hydroxide	0.79	

Volume resistivity measurements in Example 1 for a 1 μm film are on the order of $10^4 \Omega\text{-cm}$, reflectivity is 3.4%, the average optical density for the 1 μm film thickness over the region 400–700 nm is greater than 3.0, thus providing a good balance of very high optical density and electrical properties. The composition can be applied by spin coating, imaged and developed using the same process used for RGB pixels. The material has excellent shelf life (1 year in freezer; more than 3 months at room temperature). It has a low cost compared to chrome black matrix.

EXAMPLE 2

In a plastic beaker equipped with mechanical stirrer is added 31.92 g of N-methyl-pyrrolidone (NMP), 102 g of cyclohexanone, 6 g of Disperbyk-164, 26.08 g of DARC polymer (22.9% in NMP only), 30 g of Monarch 1000 and 60 g of DARC 100. The mixture is stirred at 3000 rpm for 15 minutes. This pigment slurry is then added to Eiger Mini-100 mill at 1000 rpm over a period of 15 minutes. The beaker is then rinsed with 50 g of N-methyl-pyrrolidone and rinse added to the mill. The grind speed is slowly increased to 3000 rpm. The mill is then run at 3000 rpm for 90 minutes. Formulation is then filtered through 0.2 μm filters. The formulation is summarized in Table 7.

10

(NMP) and rinse added to the mill. The grind speed is slowly increased to 3000 rpm. The mill is then run at 3000 rpm for 90 minutes. Formulation is then filtered through 0.2 μm filters. The formulation is summarized in Table 7.

TABLE 7

CHEMICAL CONSTITUENT	WEIGHT IN GRAMS
N-methyl-pyrrolidone	81.92 g
Cyclohexanone	102 g
Disperbyk-164	6 g (20% of the weight of pigment)
DARC polymer	26.08 g (22.9% in NMP only)
Monarch 1000	30 g
DARC 100	60 g

Table 8 illustrates general composition with reference to weight %.

TABLE 8

CHEMICAL COMPOSITION	WEIGHT %
Polyamic acid	10%–15%
Colorant	30%–35%
Disperseant	0.8%–1.0%
Solvent	50%–55%

Example 2 shows very high optical density, 3.6 at 1 μm film thickness over the region 400–700 nm and reflectivity of 4.1%.

EXAMPLE 3

In a plastic beaker equipped with mechanical stirrer is added 24.06 g of N-methyl-pyrrolidone (NMP), 105.84 g of cyclohexanone, 3.776 g of Disperbyk-164, 41.22 g of DARC polymer solution (22.9% solids in NMP only), 18.88 g of Monarch 1000 pigment. The mixture is stirred at 3000 rpm for 15 minutes. This pigment slurry is then added to Eiger M-100 mill at 1000 rpm over a period of 15 minutes. The beaker is then rinsed with 50 g of N-methyl-pyrrolidone and rinse added to the mill. The grind speed is slowly increased to 3000 rpm. The mill is then run at 3000 rpm for 90 minutes. Formulation is then filtered through 0.2 μm filters. The formulation is summarized in Table 9.

TABLE 9

CHEMICAL CONSTITUENT	WEIGHT IN GRAMS
N-methyl-pyrrolidone:	74.06 g
Cyclohexanone:	105.84 g
Disperbyk-164:	3.776 g (20% of the weight of pigment)
DARC polymer:	41.22 g (22.9% in NMP only)
Monarch 1000:	18.88 g

Table 10 illustrates general composition with reference to weight %.

TABLE 10

CHEMICAL COMPOSITION	WEIGHT %
Polyamic acid	15%–20%
Colorant	15%–20%
Dispersant	0.8%–1.0%
Solvent	50%–55%

Example 3 represents only pigmented formulation and does not use dye components. The dye component, particularly DARC 100, plays a particularly preferred role in

generating uniform coating (without particles or voids), creating stable dispersion and thereby increasing the shelf life of the formulation. The dyes, especially DARC 100, also serve to stabilize the polyimide coating containing such high levels of carbon black. Apparently, storage-stable polyimide coatings can not be produced when the selected dye stock is absent, at least not at the high carbon black levels required for obtaining an optical density ≥ 3.0 per micron. Furthermore, by using a polyimide vehicle for the carbon black, high resolution patterning capability is obtained (via the familiar two-layer, wet etch method) without requiring the coating to be photosensitive.

EXAMPLE 4

In a plastic beaker equipped with mechanical stirrer is added 24.06 g of N-methyl-pyrrolidone (NMP), 105.84 g of cyclohexanone, 3.776 g of dispersing agent from Table 3 (not including Disperbyk-164), 41.22 g of DARC polymer (22.9% in NMP only), 18.88 g of Monarch 1000 and 60 g of DARC 100. The mixture is stirred at 3000 rpm for 15 minutes. This pigment slurry is then added to Eiger M-100 mill at 1000 rpm over a period of 15 minutes. The beaker is then rinsed with 50 g of N-methyl-pyrrolidone and rinse added to the mill. The grind speed is slowly increased to 3000 rpm. The mill is then run at 3000 rpm for 90 minutes. Formulation is then filtered through 0.2 μm filters. The formulation is summarized in Table 11.

TABLE 11

CHEMICAL CONSTITUENT	WEIGHT IN GRAMS
N-methyl-pyrrolidone	74.06 g
Cyclohexanone	105.84 g
Dispersant (all from Table 3 except Disperbyk-164)	3.776 g (20% of the weight of pigment)
DARC polymer	41.22 g (22.9% in NMP only)
Monarch 1000	18.88 g
DARC 100	60 g

Table 12 illustrates general composition with reference to weight %.

TABLE 12

CHEMICAL COMPOSITION	WEIGHT %
Polyamic acid	15%-20%
Colorant	25%-30%
Dispersant	0.8%-1.0%
Solvent	50%-55%

Example 4 represents pigment:dye systems containing a wide variety of attempted dispersing agents (includes all from Table 2 except Disperbyk-164). Dispersants used are cationic, anionic and nonionic which generate either poor or fair dispersions with turbid or nonhomogeneous formulation indicating incompatibility or poor compatibility with polymer, solvent or pigments. The formulation of Example 4 does not generate uniform coating (with particles or voids), and has lower shelf life due to the presence of a non-compatible dispersing agent. Disperbyk-164 (BYK-Chemie, USA), a cationic dispersant composed of solution with high molecular weight blocked copolymers with groups having strong affinity to pigments, gives best results as reported in Example 1.

Method of Use

Photolithography process is applied to get fine resolution and wide β -bake window. Prime substrate is cleaned. APX-

K1, adhesion promoter from Shipley is coated on substrate at 3000 rpm for 30 seconds, baked on hot plate at 175° C. for 30 seconds. Black matrix formulation is coated on APX-K1 coated substrate at 1000 rpm for 25 seconds, α -baked to evaporate solvent on hot plate at 100° C. for 60 seconds. The coatings were then β -baked in conventional ovens at 120-180° C. for 30 minutes. The polyamic acids are 30%-50% imidized in this process. Photoresist is coated at 5000 rpm for 30 seconds, soft-baked on hot plate at 100° C. for 30 seconds, exposed at 400 mJ/cm^2 and developed. Photoresist is stripped in safestrip. Black matrix is then final cured in oven bake at 250° C. for 1 hour which completes the imidization process. Other colors are applied and processed.

Characteristic Properties

At FIG. 1, there is a flow chart explaining the manufacturing process of a black matrix according to the present invention. That is, the prime substrate is prepared at 1; the adhesion promoter is coated on the substrate at 2. The black matrix formulation is coated on the adhesion coated substrate at 3, and α -baked at 4. The coatings are then β -baked at 5. The photoresist is coated at 6, exposed at 7, and developed at 8. Photoresist is stripped at 9. The black matrix is then final cured in an oven bake at 10, thus completing the imidization process. The last step is to apply and process other colors at 11.

Industrial Applicability

The superior black matrix material of the present invention is generated having excellent heat, light and chemical resistance. The main goal of the invention is to produce a new black matrix composition having very high optical density and imaged by photolithography. This unique pattern forming material has a greatly increased processing window over conventional polyimide materials. This novel material has good durability, processability and low cost. The present invention is best suited for various display applications.

What is claimed:

1. A photolithography imageable black matrix coating material having optical density ≥ 3.0 when coated at thicknesses of 1 micron or less and having a shelf life of 90 days or more at room temperature and 365 days or more in the freezer, consisting essentially of
 - a. a polyimide precursor vehicle and a solvent system therefore;
 - b. a soluble light-absorbing dye or dye mixture, said dye or dye mixture being substantially completely soluble in the vehicle and solvent system, and being effective to absorb substantially all light across a broad spectrum of from ultra violet to infrared; and
 - c. a high performance, high color, surface treated carbon black pigment, and a suitable dispersant therefore in Newtonian dispersion.
2. The black matrix coating material of claim 1, wherein the polyimide vehicle solvent system is an effective mixture of N-methyl-2-pyrrolidone and cyclohexanone, the dye mixture is solvent brown 44 and solvent blue 67 at weight/weight ratio of 1:3 to 1:5.
3. The coating material of claim 1 wherein the pigment is Pigment Black 7 having a Color Index number 77266.
4. The coating material of claim 1 wherein the dispersant is a cationic dispersant composed of solution of high molecular weight blocked copolymers with groups having strong affinity to the pigment having Color Index number 77266 and containing no aromatics.

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5. The coating material of claim 2 wherein the polyimide vehicle is selected from the group of reaction products of

- a. oxydianiline and pyromellitic dianhydride, and
- b. oxydianiline and benzophenone tetracarboxylic dianhydride.

6. The black matrix coating material of claim 1 comprising by weight 15% to 20% polyamic acid, 50% to 55% solvent, 25% to 30% pigment and dye combined, and 0.8% to 1.0% dispersant.

7. The black matrix coating material of claim 2 having a weight percent composition of 10% to 15% polyamic acid, 50% to 55% solvent, 30% to 35% pigment and dye, and 0.8% to 1.0% dispersant.

8. The coating material of claim 1 wherein the pigment dispersion comprises pigment particles having a particle size of 0.01 to 0.2 microns.

9. The black matrix of claim 1 wherein the polyimide vehicle solvent system is an effective mixture of N-methyl-2-pyrrolidone and cyclohexanone, the dye mixture is solvent brown 44 and solvent blue 67 at weight:weight ratio of 1:3 to 5:1, the pigment has Color Index number 77266 and the dispersant is a cationic dispersant composed of solution of high molecular weight blocked copolymers with groups having strong affinity to the pigment having Color index number 77266 and containing no aromatics.

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10. A method for making an organic black matrix coating material for thin film transistor, twisted nematic, super twisted nematic, electroluminescence or plasma applications, said method comprising admixing

- a polyimide precursor vehicle and an effective solvent, and
- b. a Newtonian dispersion of a carbon black pigment having a Color Index number of 77266 and a particle size of 0.01 to 0.2 microns, and a light-absorbent organic broad spectrum light-absorbing dye or dye mixture capable of forming a black coating with an effective dispersant, in the said effective solvent, whereby the coating material's optical density is ≥ 3.0 at 1 micron or less coating thicknesses.

11. The method of claim 10 wherein the polyimide vehicle solvent system is an effective mixture of N-methyl-2-pyrrolidone and cyclohexanone, the dye mixture is solvent brown 44 and solvent blue 67 at weight:weight ratio of 1:3 to 5:1, the pigment has Color Index number 77266 and the dispersant is a cationic dispersant composed of high molecular weight blocked copolymers with groups having strong affinity to the pigment having Color index number 77266 and containing no aromatics.

* * * * *



US005587818A

United States Patent [19]

Lee

[11] Patent Number: 5,587,818

[45] Date of Patent: Dec. 24, 1996

[54] THREE COLOR LCD WITH A BLACK MATRIX AND RED AND/OR BLUE FILTERS ON ONE SUBSTRATE AND WITH GREEN FILTERS AND RED AND/OR BLUE FILTERS ON THE OPPOSITE SUBSTRATE

[75] Inventor: Si-Hyun Lee, Suwon, Rep. of Korea

[73] Assignee: Samsung Display Devices Co., Ltd., Kyungki-do, Rep. of Korea

[21] Appl. No.: 569,697

[22] Filed: Dec. 8, 1995

[30] Foreign Application Priority Data

Dec. 26, 1994 [KR] Rep. of Korea 94-36911

[51] Int. Cl. ⁶ G02F 1/1335; G02F 1/1333

[52] U.S. Cl. 349/106; 349/110

[58] Field of Search 359/68, 67

[56] References Cited

U.S. PATENT DOCUMENTS

5,442,467 8/1995 Silverstein et al. 359/68

ABSTRACT

A liquid crystal display (LCD) whose red, green and blue filters are formed on different substrates is disclosed. The LCD thus controls the width of the black matrix, enlarges the width of the filters and easily forms a color filter, having lower colorimetric purity and transmissivity than the other color filters. In an embodiment, both the blue filter and the black matrix are formed on the top glass substrate, while the red and green filters are formed on the bottom glass substrate opposite from the top substrate such that the red and green filters of the bottom substrate are aligned with the blue filter of the top substrate.

2 Claims, 4 Drawing Sheets

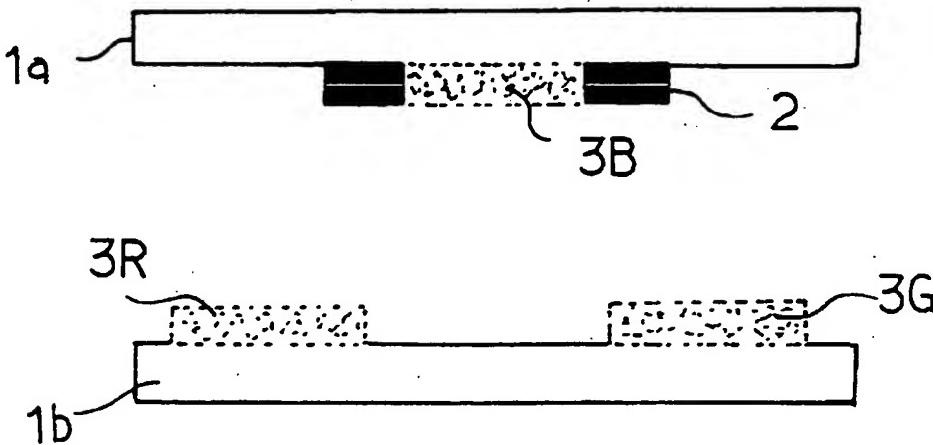


FIG.1
(PRIOR ART)

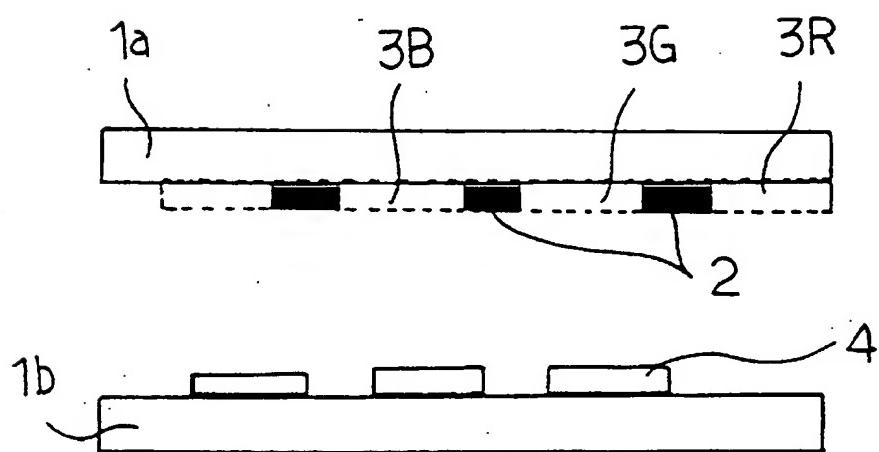
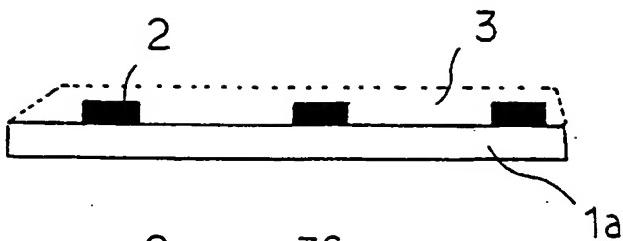
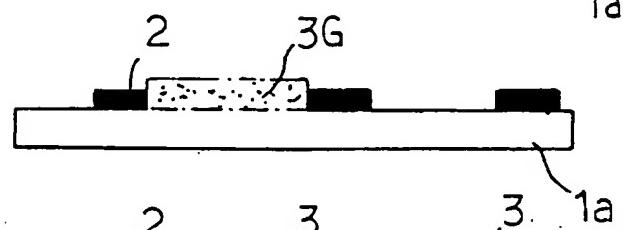


FIG.2A

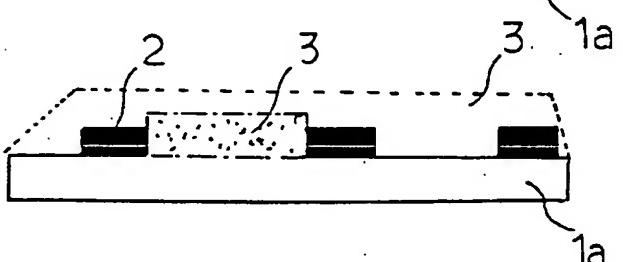
(PRIOR ART)

**FIG.2B**

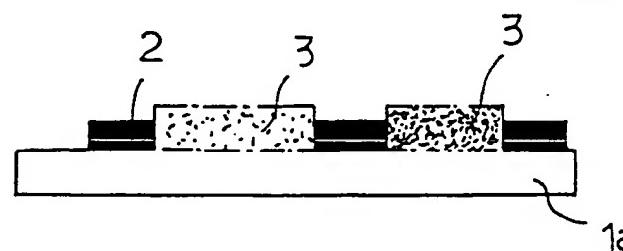
(PRIOR ART)

**FIG.2C**

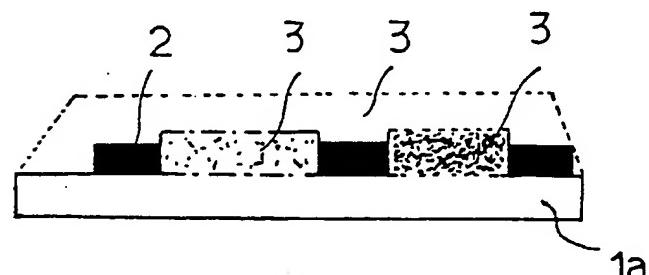
(PRIOR ART)

**FIG.2D**

(PRIOR ART)

**FIG.2E**

(PRIOR ART)

**FIG.2F**

(PRIOR ART)

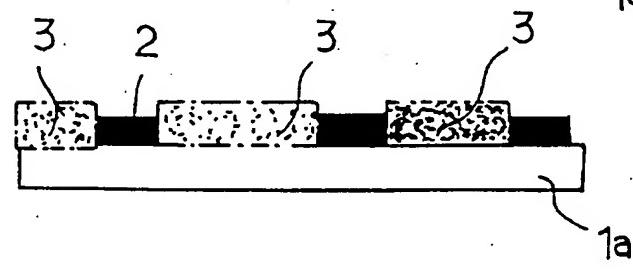


FIG.3

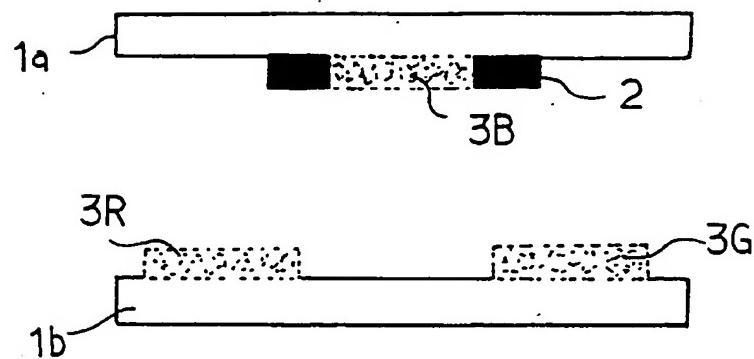


FIG.4

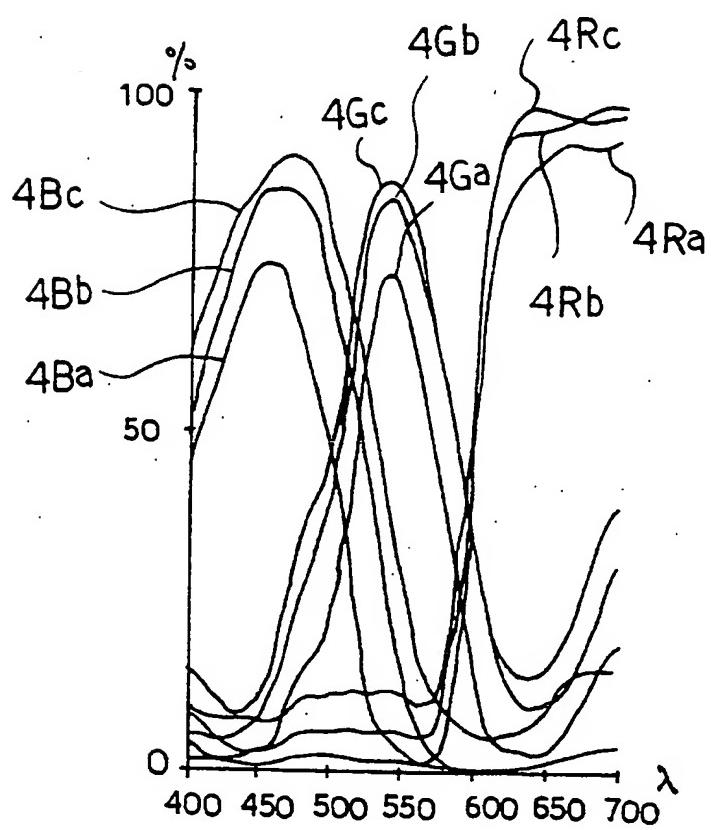


FIG.5

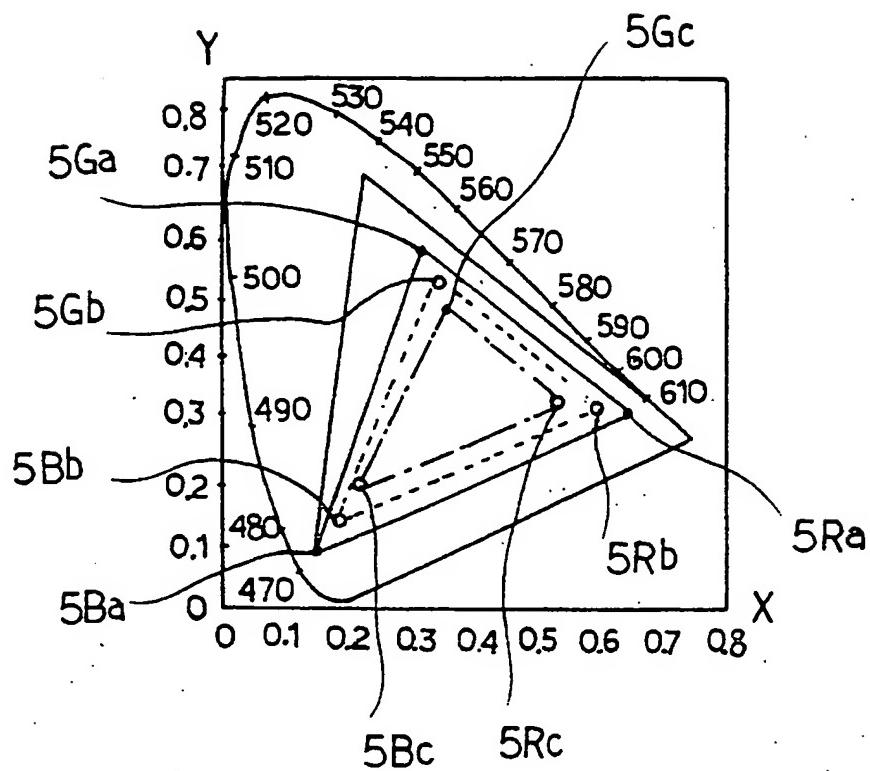
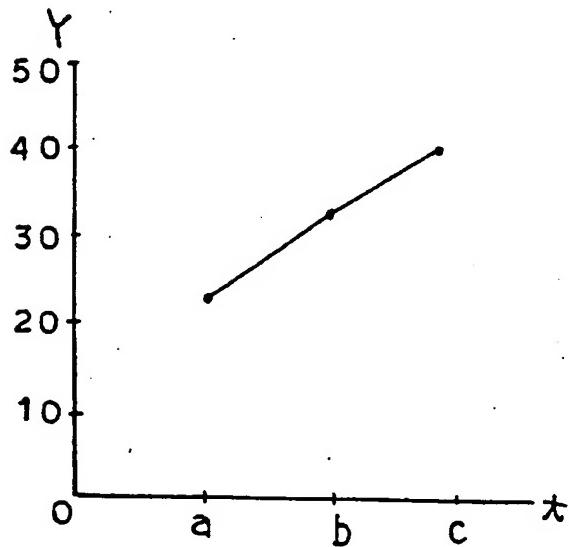


FIG.6



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THREE COLOR LCD WITH A BLACK MATRIX AND RED AND/OR BLUE FILTERS ON ONE SUBSTRATE AND WITH GREEN FILTERS AND RED AND/OR BLUE FILTERS ON THE OPPOSITE SUBSTRATE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates in general to liquid crystal displays and, more particularly, to a structural improvement in such liquid crystal displays (LCD) for easily controlling both the width of a black matrix and the size of R (red), G (green) and B (blue) filters by forming the black matrix and the R, G and B filters on different substrates. Forming of the R, G and B filters and the black matrix on different substrates also allows a color filter, having relatively lower colorimetric purity and transmissivity, to be formed separately from the other color filters thereby improving the displaying efficiency of the LCD.

2. Description of the Prior Art

FIG. 1 shows a typical liquid crystal display. As shown in the drawing, the typical liquid crystal display (LCD) includes a top glass substrate 1a. Three color filters, that is, R (red), G (green) and B (blue) filters 3R, 3G and 3B, are formed on the bottom surface of the top substrate 1a. Formed between the color filters on the top substrate 1a is a black matrix 2. The above LCD also includes a bottom glass substrate 1b opposite from the top substrate 1a. A plurality of ITO (indium tin oxide) drive electrodes 4 are formed on the top surface of the bottom substrate 1b. The above ITO electrodes 4 are aligned with the R, G and B filters of the top substrate 1a, respectively. After preparing the above top and bottom substrates 1a and 1b, liquid crystal is injected between the two substrates 1a and 1b prior to enveloping the two substrates 1a and 1b. When the ITO electrodes 4 of the above LCD are applied with a voltage, the LCD displays a color picture in accordance with intrinsic characteristics of the liquid crystal interposed between the two substrates 1a and 1b.

FIGS. 2A to 2F show a process for producing the above LCD. As shown in FIG. 2A, a light intercepting chrome layer is deposited on the top glass substrate 1a through either an electron beam deposition or a vacuum deposition. An example of vacuum deposition for forming the chrome layer is sputtering. Deposition of the light intercepting chrome layer is followed by forming of the black matrix 2. The above matrix 2 is formed through application of a photoresist, exposure with a mask, developing, wet etching, etc. Thereafter, a green filter patterning photoresist resin 3 is applied on the black matrix 2 prior to exposing with a mask. The top substrate 1a in turn is dyed with a dye having a given spectrum characteristic thereby forming the green filter 3G as shown in FIG. 2B. Thereafter, a red filter patterning photoresist resin 3 is applied on the resulting substrate 1a of FIG. 2B as shown in FIG. 2C. The substrate 1a in turn is exposed with a mask and dyed with a dye having a given spectrum characteristic thereby forming the red filter 3R as shown in FIG. 2D. A blue filter patterning photoresist resin 3 is applied on the resulting substrate 1a of FIG. 2D as shown in FIG. 2E. The substrate 1a in turn is exposed with a mask and dyed with a dye having a given spectrum characteristic thereby forming the blue filter 3B as shown in FIG. 2F. That is, the R, G and B filters are formed on the top substrate 1a in order of the G filter 3G, R filter 3R and B filter 3B.

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In the above process for forming the R, G and B filters on the substrate 1a, the green filter 3G has less bonding force for being bonded to the other colors in comparison with the other filters. Therefore, the green filter has to be primarily formed on the substrate 1a by exposing the substrate 1a with a mask after applying the green filter patterning photoresist resin on the substrate 1a. Thereafter, the red and blue filters are formed on the green filter in the same manner as described for the green filter. In the above process, it is required to carefully check both the exposing light intensity and the development due to a narrow developing margin.

However, as both the R, G and B filters and the black matrix are formed on the same plane, it is very difficult to technically reduce the area of the black matrix on a screen in view of aperture efficiency. Additionally, the G filter has an inferior bonding force for being bonded to the glass substrate because the G filter intrinsically has lower colorimetric purity and transmissivity than the other filters. In this regard, the G filter has to be formed on the glass substrate while either changing the step for forming the G filter with the other steps for forming the other filters or using a specified method.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to provide a liquid crystal display in which the above problems can be overcome and which forms the R, G and B filters on different substrates thereby controlling the width of the black matrix, enlarging the width of each filter and easily forming a filter intrinsically having lower colorimetric purity and transmissivity than the other filters.

In order to accomplish the above object, the present invention provides a liquid crystal display comprising a black matrix and a plurality of color (red, green and blue) filters formed on a pair of opposite glass substrates, wherein one or two color filters, except for the green filter, are formed on one glass substrate with the black matrix, while one or two color filters, including the green filter, are formed on the other glass substrate such that the color filter of the one glass substrate is aligned with the color filter of the other glass substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects, features and other advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a sectional view showing the construction of a liquid crystal display (LCD);

FIGS. 2A to 2F are views showing a process for producing the LCD of FIG. 1;

FIG. 3 is a sectional view showing the construction of an LCD in accordance with a preferred embodiment of this invention;

FIG. 4 is a graph showing transmissivity as a function of color filter's thickness of this LCD;

FIG. 5 is a graph showing colorimetric purity as a function of color filter's thickness of this LCD; and

FIG. 6 is a graph showing brightness as a function of color filter's thickness of this LCD.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 3 is a sectional view showing the construction of an LCD in accordance with a preferred embodiment of this

invention. As shown in this drawing, the LCD of this invention includes a black matrix 2 which is formed on the bottom surface of a top glass substrate 1a. One or two color filters (red and blue filters 3R and 3B), except for a green filter 3G, are formed on the bottom surface of the top substrate 1a. One or two color filters, including the green filter 3G, are formed on the top surface of a bottom glass substrate 1b opposite from the top substrate 1a. In this case, the filter, including the G filter, formed on the bottom substrate 1b is aligned with the filter formed on the top substrate 1a. In the preferred embodiment of FIG. 3, the B (blue) filter 3B, for example, is formed between the black matrix 2 of the top substrate 1a, while the R (red) and G (green) filters 3R and 3G are formed on the bottom substrate 1b.

FIG. 4 is a graph showing the characteristic curves of transmissivity spectrums of beams passing through the R, G and B filters of the above LCD, the transmissivity spectrums varying in accordance with color filter's thickness (thickness a>thickness b>thickness c). In the back light, blue light of 400–500 nm wavelength (λ), green light of 520–560 nm and red light of not less than 600 nm wavelength are the light components which are practically required to produce the color image of this LCD. As shown in the curves 4Ba, 4Bb and 4Bc of the graph, the blue filter 3B more reliably filters off light having a wavelength other than the range of 400–500 nm when the thickness of the filter 3B is increased. As shown in the curves 4Ga, 4Gb and 4Gc of the graph, the green filter 3G more reliably filters off light having a wavelength other than the range of 500–560 nm when the thickness of the filter 3G is increased. The blue filter 3B more reliably filters off light having a wavelength of less than 600 nm when the thickness of the filter 3R is increased as shown in the curves 4Ra, 4Rb and 4Rc of the graph.

FIG. 5 is a graph showing colorimetric purity as a function of color filter's thickness (a>b>c) of this LCD. In the CIE chromaticity diagram of FIG. 5, the chromaticity points 5Ra, 5Rb and 5Rc are the chromaticity coordinates of light passing through the red filter (a>b>c). The chromaticity points 5Ga, 5Gb and 5Gc are the chromaticity coordinates of light passing through the green filter (a>b>c). The chromaticity points 5Ra, 5Rb and 5Rc are the chromaticity coordinates of light passing through the red filter (a>b>c). As shown in the graph of FIG. 5, the chromaticity coordinates of the light passing through the color filters 3R, 3G and 3B approximate to those of the CIE chromaticity diagram in proportion to the thickness of the color filters 3R, 3G and 3B. Therefore, the chromaticity purity of the LCD is improved in proportion to the color filter's thickness.

FIG. 6 is a graph showing brightness as a function of color filter's thickness (a>b>c) of the above LCD. As shown in this graph, the brightness (Y) is reduced in inverse proportion to the color filter's thickness.

The operational effect of the above LCD will be described herein, below.

In the above LCD, one or two color filters, except for the green filter 3G, are formed on the top substrate 1a with the black matrix 2, while one or two color filters, including the G filter 3G, are formed on the bottom glass substrate 1b. In this case, at least one filter, including the G filter, formed on the bottom substrate 1b is aligned with at least one filter formed on the top substrate 1a. That is, the green filter 3B and the black matrix 2 are formed on different substrates. In addition, the color filters 3R, 3G and 3B are formed on different substrates. It is thus possible to control the width of the black matrix 2. The R, G and B filters are less limited by

area when forming the filters on the substrate thereby increasing the area ratio of the color filters in the LCD. Additionally, a gap is formed between the R, G and B filters 3R, 3G and 3B and the black matrix 2 since there is a cell gap of 6–7 μ between the top and bottom glass substrates 1a and 1b. Therefore, the above LCD not only improves the aperture efficiency, but also enlarges the visible angle in accordance with diffraction of light. The green filter 3G having a lower bonding force than the other color filters 3R and 3B is formed on one glass substrate, while at least one of the other color filters is formed on the other glass substrate. That is, the green filter 3G and the other filters 3R and 3B are formed on different substrates. The color filters 3R, 3G and 3B of this LCD can be thus formed on the substrates in disregard of the conventional processing order of the green filter, red filter and blue filter.

In the LCD of this invention, the transmissivity of the LCD is improved in inverse proportion to the color filter's thickness (a>b>c) as shown in the graph of FIG. 4. The chromaticity purity of the LCD is improved in proportion to the color filter's thickness as shown in the graph of FIG. 5. The brightness of the LCD is improved in inverse proportion to the color filter's thickness as shown in FIG. 6. Therefore, the transmissivity, chromaticity purity and brightness of the green filter 3G, which are intrinsically lower than those of the other filters 3R and 3B, can be easily controlled by changing the thickness of the green filter 3G relative to the other filters 3R and 3B.

As described above, the present invention provides an improved LCD. In the above LCD, one or two color filters, except for the green filter, are formed on one glass substrate with the black matrix, while one or two color filters, including the green filter, are formed on another glass substrate. It is thus possible to control both the width of the black matrix and the size of the color filters. One color filter, intrinsically having lower chromaticity purity and transmissivity than the other color filters, is formed separately from the other color filters. The above LCD thus easily compensates for the characteristics of the one color filter having the lower chromaticity purity and transmissivity. As the one color filter is formed separately from the other color filters, the color filters of this LCD can be thus formed on the glass substrates in disregard of the conventional processing order of the green filter, red filter and blue filter, thereby easily producing the LCD.

Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

What is claimed is:

1. A liquid crystal display comprising a black matrix and a plurality of color (red, green and blue) filters formed on a pair of opposite glass substrates, wherein filters of one or two colors other than green, are formed on one glass substrate with said black matrix, while filters of two or one color, respectively, including said green filter, are formed on the other glass substrate such that the edge of the color filters of the one glass substrate are aligned with the edge of the color filters of the other glass substrate.

2. The liquid crystal display according to claim 1, wherein said red and blue filters are formed on the one glass substrate with said black matrix, while said green filters are formed on the other glass substrate.



US005780201A

United States Patent [19]**Sabnis et al.****[11] Patent Number:** **5,780,201****[45] Date of Patent:** **Jul. 14, 1998**

[54] ULTRA THIN PHOTOLITHOGRAPHICALLY IMAGEABLE ORGANIC BLACK MATRIX COATING MATERIAL

[75] Inventors: Ram W. Sabnis; Jonathan W. Mayo; Edith G. Hays; Terry L. Brewer, all of Rolla; Michael D. Stroder, Springfield, all of Mo.; Akira Yanagimoto, Tokyo, Japan; Yasuhisa Sone, Chiba, Japan; Yoshitane Watanabe, Tokyo, Japan; Kiyomi Ema, Chiba, Japan

[73] Assignees: Brewer Science, Inc., Rolla, Mo.; Nissan Chemical Industries, Ltd., Chiyoda-ku, Japan

[21] Appl. No.: **721,841**

[22] Filed: **Sep. 27, 1996**

[51] Int. Cl.: **G03F 7/004**

[52] U.S. Cl.: **430/270.1; 430/7**

[58] Field of Search 430/270.1, 283.1,
430/7; 349/110

[56] References Cited**U.S. PATENT DOCUMENTS**

4,822,718 4/1989 Latham et al. 430/271.1
5,527,649 6/1996 Sato et al. 430/7
5,619,357 4/1997 Angelopoulos et al. 349/110

Primary Examiner—John A. McPherson
Attorney, Agent, or Firm—Veo Peoples, Jr.

[57] ABSTRACT

An organic black matrix having high resistivity ($\geq 10^{11}$ ohm/square), high optical density (≥ 2.0) at ultra thin film thicknesses (≤ 1.0 microns) for improved STN and TFT pixel display applications is made possible by combining polyimide/dye solutions and mixed metal oxide pigment dispersions at a weight/weight ratio of dye to pigment of 1:15 to 3:15. The need for low resistivity carbon black, as a replacement for sputtered chrome, is negated.

10 Claims, 6 Drawing Sheets

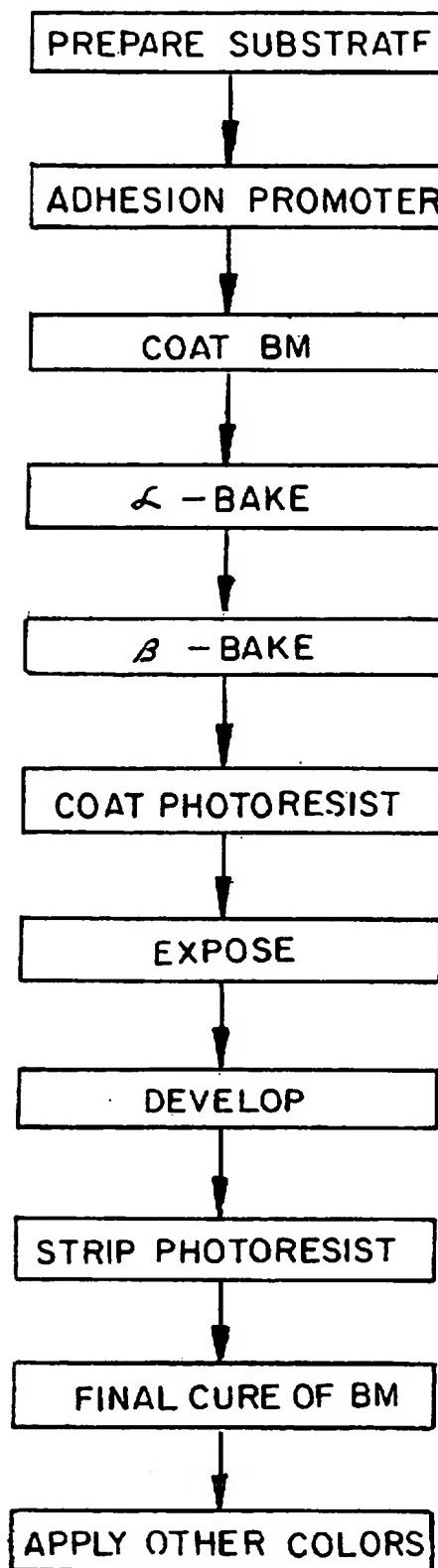
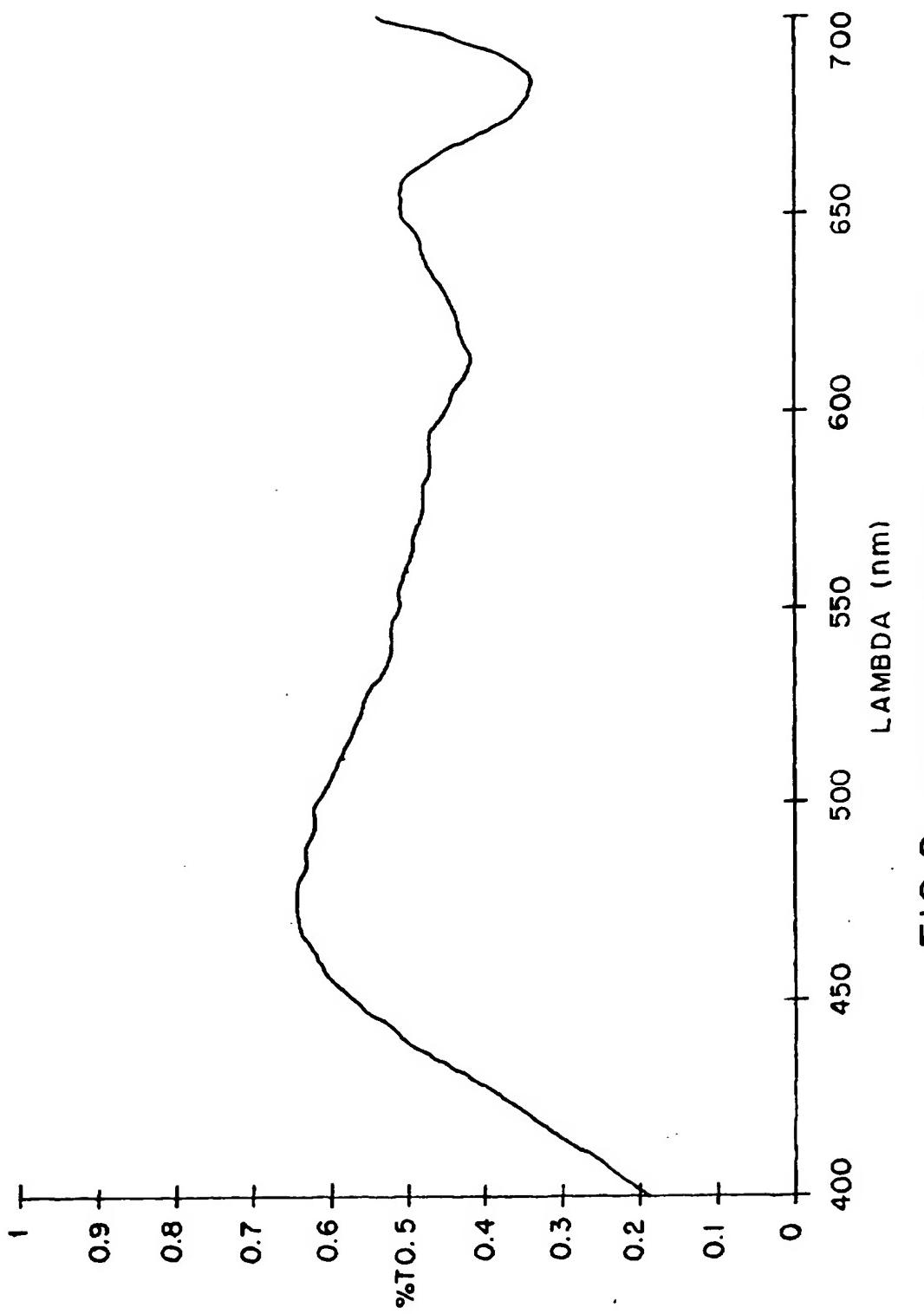


FIG. 1 Flow Chart of Manufacturing Process of BM

FIG. 2 TRANSMISSION OF 1 μ m FILM

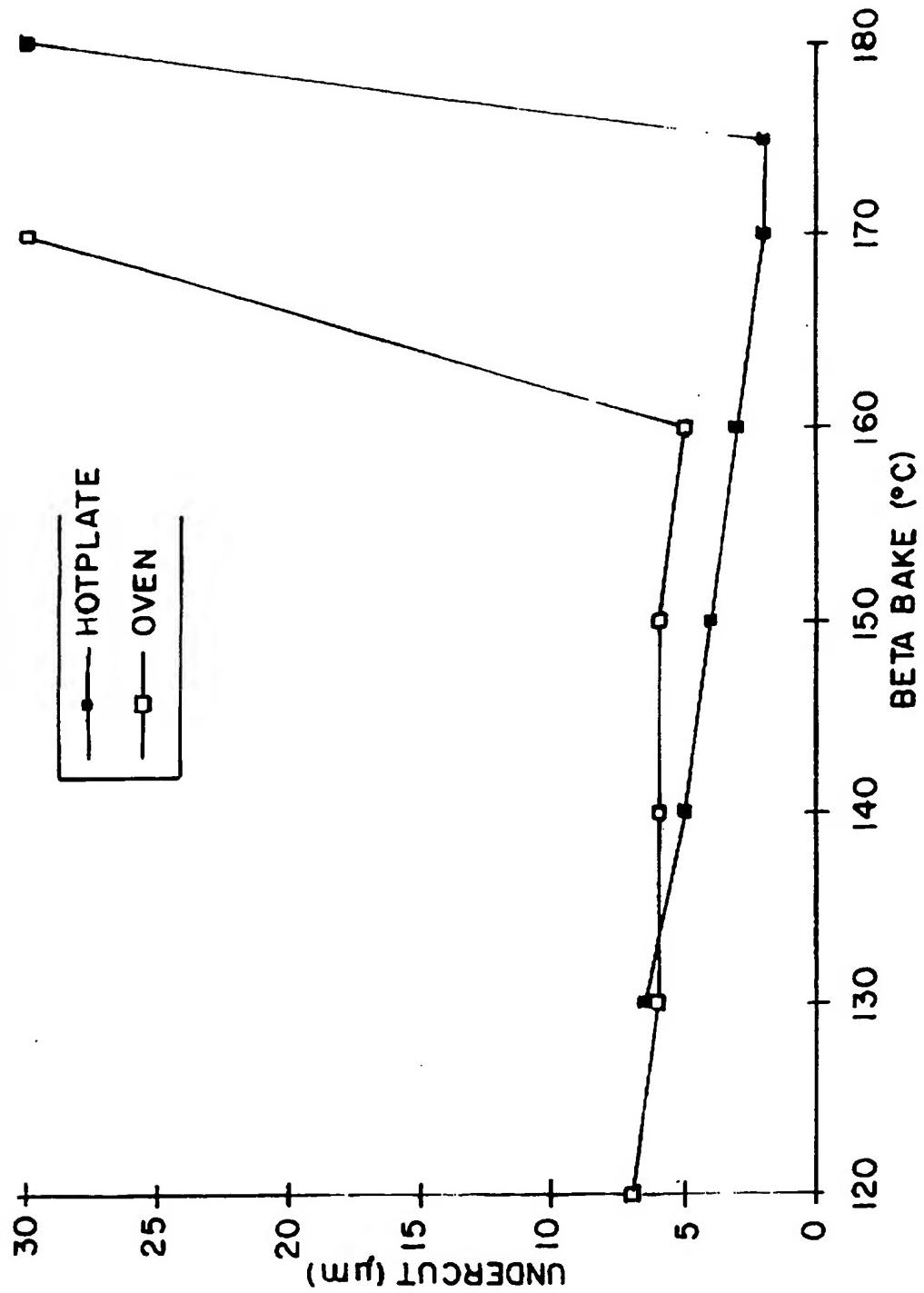


FIG. 3 LITHOGRAPHY DATA

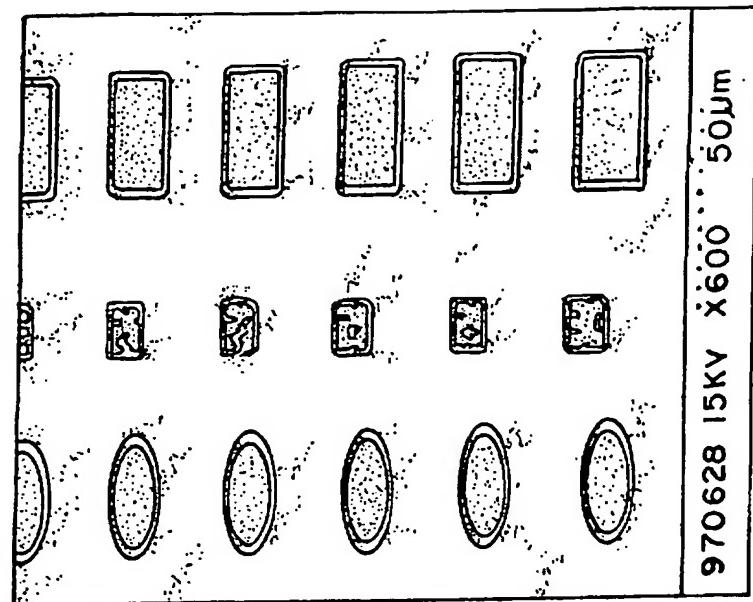


FIG.5 SCANNING ELECTRON
MICROSCOPE DATA

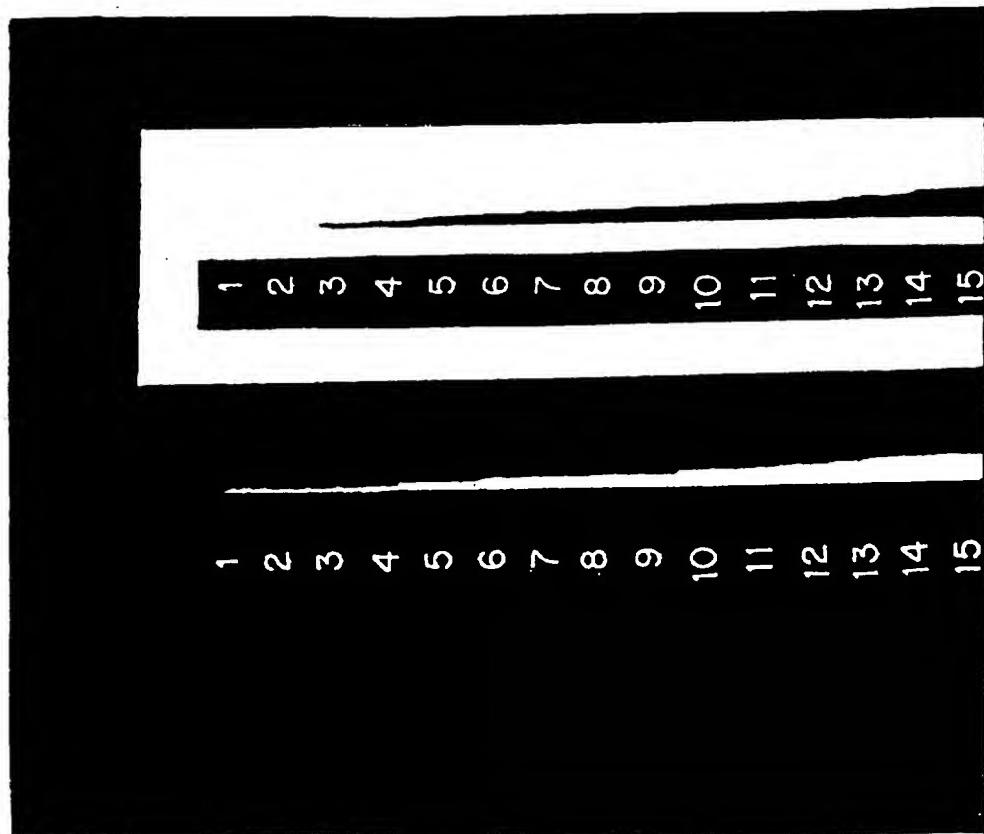


FIG.4 RESOLUTION PATTERN

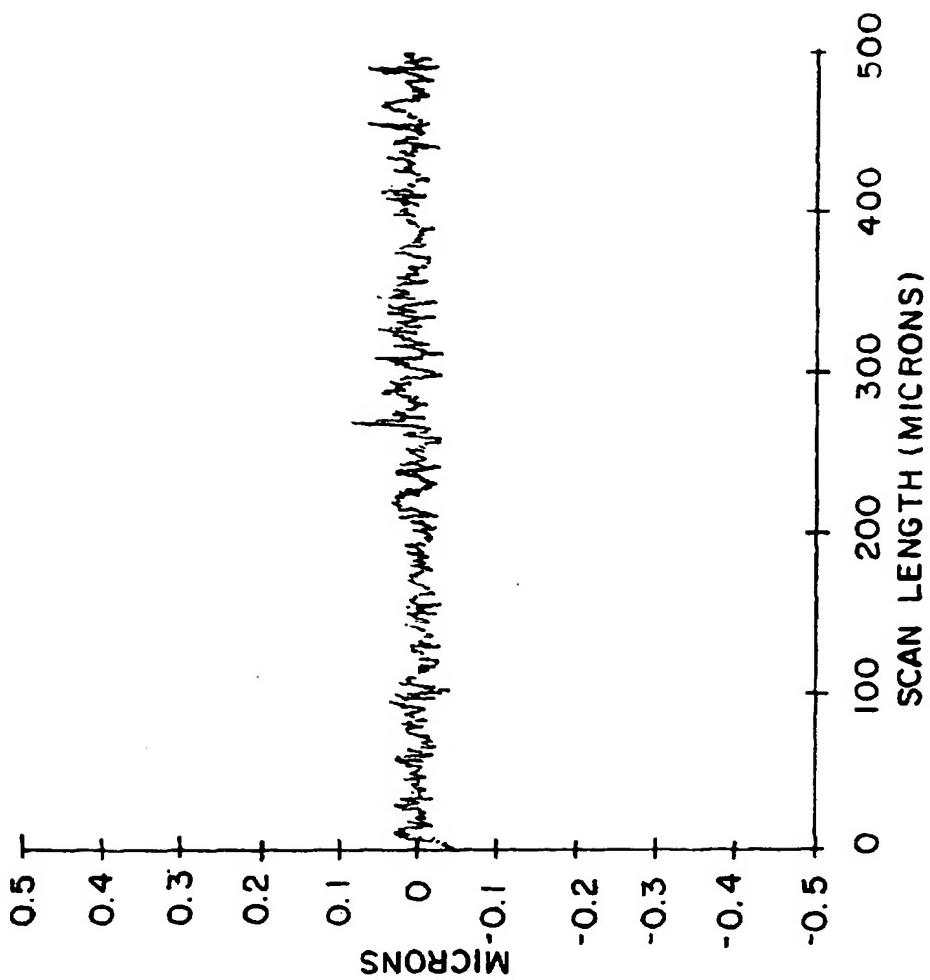


FIG. 6 SURFACE ROUGHNESS MEASUREMENT

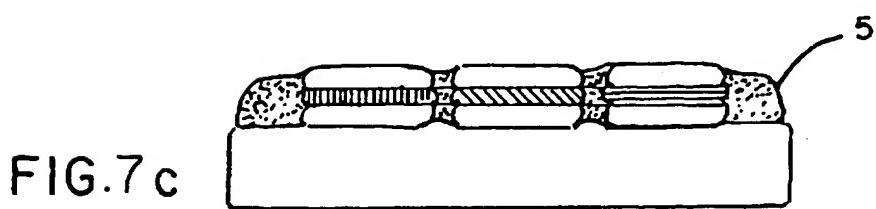
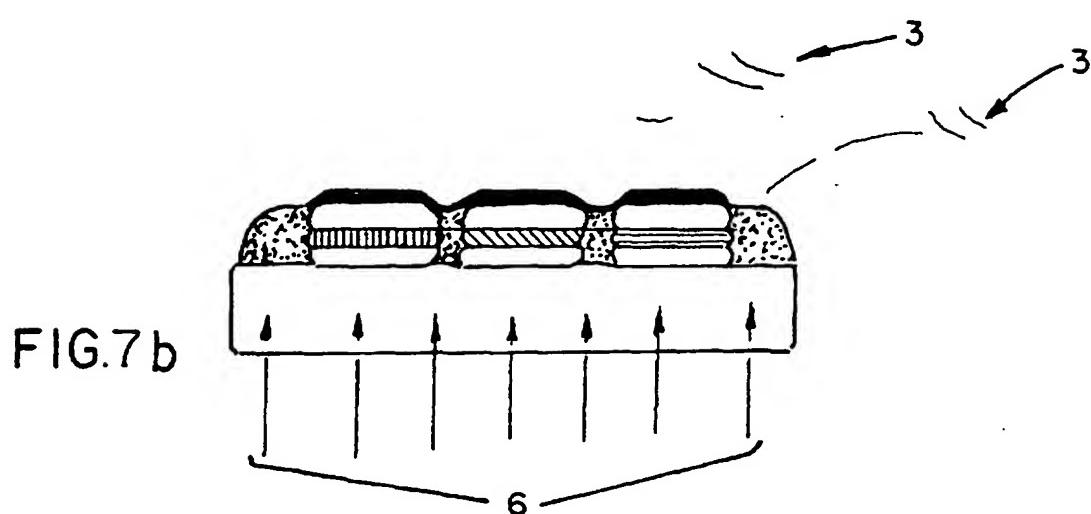
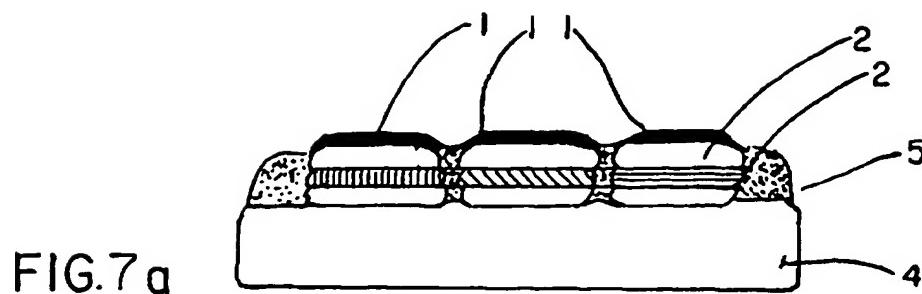


FIG. 7 THE SELF-ALIGNMENT PROCESS
USED TO FORM THE BLACK MATRIX

ULTRA THIN PHOTOLITHOGRAPHICALLY IMAGEABLE ORGANIC BLACK MATRIX COATING MATERIAL

BACKGROUND OF INVENTION

1. Field of Invention

The present invention relates to organic black matrices for color filter plate manufacture and to methods for making the same. It particularly relates to nonconductive black matrices, having very high resistivity, and having high optical density at ultra thin film thicknesses.

2. Background of the Prior Art

Multicolor liquid crystal displays (LCDs) are routinely produced having a thin, light-absorbent film, called a black matrix, applied to an array of color pixels which together form a color filter plate. The processing of such color filter plates remains one of the most troublesome steps during mass production of the LCDs because they use sputtered chrome black matrices.

A spincoatable, organic polymer based black matrix would tend to be more environmentally friendly than chrome, easier to reproduce, and offer lithographic processing advantages. However, there are at least two types of color filter plates for LCDs where organic polymer black matrices are woefully expensive and/or lack the desired performance. That is, the unavailability of an organic black matrix photoresist having sufficiently high resistivity and sufficiently high optical density at ultra thin film thickness, has hampered the advancement of 1) thin film transistor (TFT)-arrays for TFT-LCDs and 2) super twisted nematic (STN) LCDs.

For purposes of illustration, FIGS. 7, 7(a), 7(b), and 7(c) show a somewhat oversimplified stepwise illustration of the coating and imaging of organic black matrix photoresists onto either TFT or STN color pixels for large area LCDs. The RGB (red, green, blue) color pixels 1 could be either TFTs or STNs. Such color filter plates have an Indium-tin-oxide (ITO) electrode layer or layers 2 and signal lines 3. All are normally applied to a glass substrate 4. The illustration shows the exposure of UV light through the glass substrate for purposes of lithographically imaging the organic black matrix 5.

In these TFT and STN applications, high resistivity (so as to be nonconductive) is mandatory in order to avoid electrical coupling between the ITO electrode layer and the signal lines. Otherwise, coupling with the signal lines (sometimes referred to as data lines) causes vertical crosstalk.

The optical density (O.D.) of the black matrix must be greater than 2.0 in order to block the transmission of light to the TFT or STN displays. Otherwise, photo leaks from non-display areas will reduce the contrast ratio and create adverse photo leakage current. In other words, one can enhance the contrast of the LCD by eliminating the light leakage which would otherwise occur through spaces patterned between the red, green, and blue (RGB) pixels on the color filter plate. The technical goal is to keep the light transmission at or below 1% across the entire spectrum of from ultraviolet to infrared, at ultra thin black matrix film thicknesses.

It has proven extremely difficult, if not impossible, to manufacture a nonconductive organic black matrix having an O.D. greater than 2.0 at ultra thin black matrix film thicknesses. Although O.D. greater than, or equal to, 2.0 have been achieved for organic black matrices at a 2 micron

polymer thickness, such layer thicknesses are at the threshold for a number of defects. For example, the so-called reverse tilt inside each pixel display area occurs at 2 microns. Reverse tilt causes after-image and contrast deterioration. Overcoming that drawback, inter alia, requires a nonconductive, organic black matrix film having O.D. greater than 2.0 at a thickness of 1.0 micron or less.

Despite the high cost-of-ownership, a complex manufacturing process (sputtering), and potential environmental problems, and despite a higher reflectance than desired, the most common black matrix material has continued to be sputtered chrome, rather than spin-coated organic polymers. Although vacuum evaporation and other coating techniques for metals such as nickel and aluminum and even chromium have been devised, sputtered chrome remains the most common technique and material because other techniques and other materials lack sufficiently high O.D. (>2.0) to provide enhanced contrast and high resolution, at sufficiently ultra thin thicknesses (1 micron or less) and at sufficiently high resistivity (at least 10^5 ohm/square) to be commercially effective for STN and TFT application.

For example, Latham's U.S. Pat. No. 4,822,718 disclosed in 1989 potential black matrices of the organic type made from polyamic acid/dye combinations (as distinguished from pigment-dispersions). The resistivity of these light-absorbing layers was found to be as high as 3.0×10^{15} ohm/square.

It has been disclosed by Hessler, et al., in the article "Pigment-Dispersed Organic Black-Matrix", *SID Digest*, 26:446, (1995), however, that Latham's mixtures of the red and blue dyes bound in polyimide composition as well as mixtures of red and blue pigments in pigment-dispersed organic black matrices disclosed by others did not come close to the desired O.D. (greater than 2.0), even when coated at film thicknesses greater than 3 microns. Changing the ratios of red to blue pigments, or adding low levels of violet, yellow or green pigments to the red and blue pigment mixtures did not improve overall O.D. performance of the formulations. Carbon black pigment, dispersed in acrylic polymer, did, however, achieve 0.01% light transmission for some samples. An average O.D. of 2.8 for a 1.5 micron, spin-coated film, over the whole spectrum of 400-700 nm, was made possible by a critical selection of dispersants. However, the resistivity was a disappointing 90K ohm/square.

As disclosed by Yamanaka in his article, "Integrated Black Matrix on TFT Arrays", *SID Digest*, 23:789 (1992), carbon black, even with an advanced acrylic photo polymer, does not achieve O.D. greater than 2.0, at thicknesses less than 2 microns without sacrificing resistivity and creating crosstalk. Yamanaka also describes the disadvantage of a 2 micron "step size" (or thickness). It is so large that it results in reverse tilt.

U.S. Pat. No. 5,368,976, by Tajima, et al., discloses another example of pigment-dispersed color filter compositions. An alkali-soluble block copolymer is employed as a binder for a radiation-sensitive compound and pigments such as pigment Black 1 and pigment Black 7 but with unsuitably large particle sizes (filtered at 10 microns). Although it is well known that pigment Black 1 does not provide the requisite O.D. greater than 2.0 at practical thicknesses, pigment Black 7 (better known as simply "Carbon Black") does provide O.D. greater than 2.0 as shown by Hessler, et al. Yet, as Yamanaka explains, even at thicknesses less than 2.0 microns, the threat of crosstalk exists when the black matrix is too conductive for effective STN or TFT

applications, and particle sizes of 10 micron diameter would lead to films having reverse tilt.

Suginoya, et al., in their article "Self-Alignment Fabrication of the ITO Electrode Pattern on an Electrodeposited Tricolor Filter in a Black Matrix: An Application to STN-LCDs". *Proc. of SID*, 32:201, (1991), identify another shortcoming of STN-LCDs having organic black matrices made from carbon black. That is, although the green filter of the display provides a good shutter which transmits less than 1% of incident light at 365, 405 and 435 nm, the red filter does not. It has transmittance of 4% at 365 nm and 6% at 405 nm. Also, the blue filter is even worse, having transmittance of 35% at 405 nm and of 55% at 435 nm. A separate approach was therefore necessary for light above 400 nm than for light below 400 nm. The black matrix average transmittance was substantially greater than 1.0% throughout the spectrum, when using this complicated approach (FIG. 13 of the reference). It was closer to 10%.

Accordingly, neither the past dye-based nor the past pigment-based organic black matrices could effectively provide O.D. greater than 2.0, at thicknesses less than 1 micron without disaffecting STN and TFT performance. Furthermore, although the dye-based black matrices have the requisite resistivity to provide improved avoidance of crosstalk from electrical coupling between ITO electrodes and signal lines, the substitution of sufficient dye mixtures for a portion of the pigment-dispersed material needed to raise its resistivity beyond 10^5 ohm/square would be expected to weaken the O.D. to below 2.0 unless a film thickness greater than 2.0 microns was applied to the pixels and substrate. Only Carbon Black (Pigment Black 7) with its low resistivity of 90×10^2 ohm/square comes close to O.D. 2.0 at 1.5 micron thickness.

It would therefore be highly unexpected that any combination of dye-based and pigment-based organic black matrices, other than Carbon Black, would provide improved O.D. of over 2.0, without requiring a film thicker than 2.0 microns and Carbon Black is too conductive for effective STN and TFT application. The vast difference in resistivity of carbon black pigment versus various organic dyes would lead one to believe that any appreciable amount of such pigment added to the dyes in order to effectively increase O.D. beyond 2.0 would be significantly detrimental to the resistivity per unit volume of the final material. Yet other pigments have had too low an O.D. to even be considered for ultra thin black matrices.

It is an object of the present invention to provide a stable organic black matrix having O.D. greater than 2.0, at thicknesses less than 1 micron but surface resistivity greater than 10^5 ohm/square.

SUMMARY OF THE INVENTION

The present invention fulfills the above-stated objective and others by a synergistic composition of polyimide-dye-pigment. The black matrix of this invention has high resistivity and an O.D. greater than 2.0 at a film thickness of 1 micron or less.

The material patterns on various display applications have excellent evenness, high strength, superior environmental safety, high stability, good shelf-life and a low cost of production.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow chart explaining the manufacturing process of a black matrix according to the present invention.

FIG. 2 is a graph showing transmission spectra of 1 μm cured film obtained in Example 1.

FIG. 3 shows sets of lithography data using both convection oven and hot plate beta-bake processes.

FIG. 4 is a schematic diagram illustrating photo of a resolution dagger.

FIG. 5 demonstrates Scanning Electron Microscope (SEM) of the black matrix material after resist removal and final cure.

FIG. 6 is a schematic diagram illustrating typical surface roughness measurement of the cured film.

FIGS. 7(a), 7(b), and 7(c) illustrate coating and imaging organic black matrices photoresist onto generally STN or TFT color pixels for large area LCDs.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention fulfills the above-stated objective and others by a synergistic composition of polyimide-dye-pigment black matrix mixtures. Such black matrix compositions preferably comprise, by weight, 4% to 8% polyimide binder, 9% to 13% colorant (dye plus pigment), 80% to 85% solvent and 0.3% to 0.8% dispersant. The weight/weight ratio of dye: pigment will range from about 1:15 to about 3:15, preferably 2:15. Surprisingly, the combined O.D. of organic dyes plus non-carbon black pigments is greater than the sum of their parts at less than 1.0 micron (hereinafter referred to as ultra thin) film thickness.

POLYIMIDE/DYE

The polymer vehicles, for the black matrix compositions of the present invention, will typically include polyimide precursors which react in situ to form polyimide resins. Preferably, the precursors will consist of a polyamic acid prepared by reacting oxydianiline (ODA) with pyromellitic dianhydride (PMDA) or by reacting ODA with PMDA and/or benzophenone tetracarboxylic dianhydride (BTDA). These components are typically employed in approximate stoichiometric amounts. Other suitable polyamic acids and polyamic precursors typically employed for the polyimide vehicles of this invention are conventional components as, for example, those listed in Table 1 below. Note that it is possible to include water soluble polymers such as polyvinyl/pyrrolidone and other conventional resins such as novolac in admixture with these precursor components without departing from the Applicants' definition of polyimide precursors.

TABLE 1

Diamines	Dianhydrides
p-Phenylenediamine	3,3',4,4'-Benzophenone tetracarboxylic dianhydride
m-Phenylenediamine	Pyromellitic dianhydride
3,3'-dimethoxy-4,4'-diaminobiphenyl	3,3',4,4'-Biphenyl tetracarboxylic dianhydride
1,4-bis(4-aminophenoxy)benzene	4,4'-Oxydiphenolic anhydride
4,4'-Bis(4-aminophenoxy)biphenyl	3,3',4,4'-Diphenylsulfone tetracarboxylic-dianhydride
Bis-4-(4-aminophenoxy)phenyl)ether	1,2,3,4-cyclobutane tetracarboxylic-dianhydride
4,4'-Oxydianiline	4,4'-Diaminodiphenyl sulfone
4,4'-Diaminodiphenyl sulfone	2,2-Bis[4-(4-aminophenoxy)phenyl]sulfone
2,2-Bis[4-(4-aminophenoxy)phenyl]sulfone	4,4'-Bis[hexafluoroisopropylidene]diphthalic anhydride

The dye components of the present invention are soluble organic dye combinations which can effectively absorb light

over the broad spectrum of infrared to ultraviolet. It is critical that the dyes be soluble in solvents which dissolve the polyimide vehicle (which solvents will be discussed later). In a particularly preferred embodiment of the present invention, a weight/weight ratio of from about 1:3 to 1:5 of Orasol brown 6RL (Solvent brown 44) to Orasol blue GN (Solvent blue 67) provides a surprisingly effective component for this invention. Such a mixture is commercially available under the trade name DARC-100 sold by Brewer Science, Inc.

Other combinations of Blue, Red, Orange, etc., dyes capable of producing high resistivity black coatings in U.S. Pat. No. 4,822,718 may be employed.

In a preferred embodiment of the present invention, all of the dye component together with a substantial amount of the polyimide component (at least 50%) may be provided in accordance with the black coating compositions disclosed in U.S. Pat. No. 4,822,718, which patent is herein incorporated-by-reference to this disclosure.

Highly preferable dyes for the present invention may also include dyes specified from the color index of Solvent Black 3 to Solvent Black 47, more particularly Solvent Black 35 (Zapon Black X50, BASF), Solvent Black 27 (Zapon Black XS1, BASF), Solvent Black 3 (Neptun Black X60, BASF), Solvent Black 5 (Flexo Black X12, BASF), Solvent Black 7 (Neptun Black NB X14, BASF), Solvent Black 46 (Neptun A Black X17, BASF), Solvent Black 47 (Neopin Black X58, BASF), Solvent Black 28 (Orasol Black CN, Ciba-Geigy), Solvent Black 29 (Orasol Black RL, Ciba-Geigy), and Solvent Black 45 (Savvinyl Black RLS, Sandoz Corp.).

PIGMENT-DISPERSIONS

One surprising aspect of the present invention is the ability to obtain optical density >2.0 at ultra thin film thicknesses without having to resort to the use of Carbon Black.

Although the pigments employed in this invention are indeed macroscopic particles having high surface area and a strong tendency to flocculate which can create haze and light scattering aggregates or variations in rheology, when the pigments of this invention are suitably dispersed and admixed with the polyimide/dye solutions, excellent evenness is achieved.

The pigments of this invention are mixtures of inorganic metal oxides or mixtures of multiple metal oxides selected from metal oxides of copper, manganese, chromium, iron, magnesium, aluminum, tin, zinc, titanium, nickel, cobalt and mixtures thereof. These metal oxides are preferred for purposes of forming the so-called spinel structure. They unexpectedly provide a synergy that together with dyes of this invention will achieve O.D. >2.0 at ultra thin film thicknesses, while their combined surface resistivity is magnitudes above the 10⁵ ohm/square threshold required for effective STN and TFT application.

Suitable pigments may include pigments specified from color index 77248 to 77494, including pigment Black 22 (color index (C.I.) 77429), such as Fast Black 100 sold by Bayer Corp.; Pigment Black 26 (C.I. 77494) such as Daiyroxide TM Black 3550 and 3551 sold by Dainichiseika Color & Chemical Manufacturing Co., Ltd. of Japan; Pigment Black 27 (C.I. 77502); Pigment Black 28 (C.I. 77428), sold as Harshaw 9875 M Plus by Engelhard Corporation; and also mixtures of Pigment Green 50 (C.I. 77377) with Pigment Blue (C.I. 77346), and Pigment Red (C.I. 77491). It is particularly preferred to use Pigment Black 26 (C.I. 77494) composed of mixed metal oxide of copper, manganese and iron.

It is preferred in manufacturing the pigment dispersions of this invention to employ as the primary particle size of the pigments less than 100 nanometers (nm), particularly less than 50 nm. The particles of these pigments may also be coated with inorganic layers of silica, alumina, or zirconia for purposes of improving the stability of the dispersions.

Dispersants, effective for a Newtonian dispersion of the pigment in the polyimide vehicle and solvent system, were desired. Cationic dispersants are preferred, particularly cationic dispersants composed of solutions with high molecular weight blocked copolymers with chemical groups having strong affinity to the pigments of this invention. One such particularly preferred dispersant is that sold under the trademark Disperbyk-163 by Byk-Chemie. Other such cationics include, for example, the trade names Disperbyk-160, 161, 162, 164 and 166. Anionic and nonionic dispersants are also suitable. A list of such dispersants may be seen in Table 2 below.

TABLE 2

	Dispersing Agent	Company	Ionic Nature
25	Disperbyk-160	Byk-Chemie	Cationic
	Disperbyk-161	Byk-Chemie	Cationic
	Disperbyk-162	Byk-Chemie	Cationic
	Disperbyk-163	Byk-Chemie	Cationic
	Disperbyk-164	Byk-Chemie	Cationic
	Disperbyk-166	Byk-Chemie	Cationic
	Lactimon	Byk-Chemie	Anionic
	Bykumen	Byk-Chemie	Anionic
30	Dumasperse 535	Hickson	Anionic
	Dumasperse 540	Hickson	Anionic
	Dumasperse 545	Hickson	Anionic
	Mazisperse 85B	PPG	Nonionic
	Mazisperse SF 19	PPG	Nonionic
35	Nuosperse 657	Huls	Nonionic
	Nuosperse 700	Hul	Anionic
	Solsperse 12000	Zeneca	Anionic
	Solsperse 27000	Zeneca	Nonionic

40 The dispersion is carried out in, for example, Eiger Mini-100 motormills using suitable beads, e.g., 0.65 mm yttrium stabilized zirconium oxide beads.

Preferably, the pigments are dispersed in a Newtonian dispersion having dispersant in an amount comprising 5% the weight of the pigment, a solution of polyimide precursor (22.7% solids in solution) and a substantial amount of solvent.

SOLVENTS

50 A solvent effective for solubilizing the polyimide vehicle and dye compound is selected. The most preferred solvents for the polyimide/dye component and for the pigment dispersion are N-methyl-2-pyrrolidone (NMP) and cyclohexanone. Other suitable solvents may include dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), bis-2-methylethyl ether (diglyme), tetrahydrofurfuryl alcohol (THFA), dimethylsulfoxide (DMSO), xylenes, cyclic ketones, alcohols, esters, ethers and mixtures thereof. A polymer/dye solution of such dyes shall also be suitable for the effective pigment dispersion, previously discussed.

55 The black matrix compositions of this invention (1) can be applied to substrates by spin coating, (2) can be imaged using the same process employed to image the RGB pixels, (3) developed using the same development process as the pixels, and (4) provide an average O.D. for 1 micron film thicknesses over the region 400–700 nm of 2.4 O.D. The shelf life is excellent, i.e., three months in the freezer or

three weeks at room temperature. The surface resistivity is very high, i.e., in the range of 10^{11} ohm/square, and cost of production is much lower than sputtered chrome black matrices.

EXAMPLE 1

In a plastic beaker is added 11.6 g of N-methylpyrrolidone (NMP), 82 g of cyclohexanone, 1.5 g of dispersylk-163, 20 g of DARC polymer and 30 g of Pigment Black 26. The mixture is stirred with a spatula for about 5 minutes till homogeneous. This pigment slurry is then added to Eiger M-100 mill at 1000 rpm over a period of 15 minutes, using 0.65 mm yttrium stabilized zirconium oxide beads. The beaker is then rinsed with 20 g of cyclohexanone and rinse added to the mill. The grind speed is slowly increased to 3000 rpm. The pigment is ground at this speed for 2 hours. In a separate plastic beaker equipped with mechanical stirrer is added 32.4 g of DARC polymer (22.9% in NMP only) and 60 g of DARC 100. The mixture is stirred for 10 minutes. After 2 hours, the mixture of DARC polymer and DARC 100 is added to the mill at 1000 rpm. DARC polymer is synthesized by dissolving 48.1 g of oxydianiline in NMP, then added 51.8 g of pyromellitic dianhydride and reacted for 5 hours at 40° C. The beaker is rinsed with 50 g of N-methyl-pyrrolidone and the rinse is added to the mill at 1000 rpm. The mill is then run at 3000 rpm for 90 minutes. Formulation is then filtered through 0.2 µm filters. The formulation is summarized in Table 3. A resistivity of 5.6×10^{11} ohm/square, at a thickness of 1 micron and an O.D. of 2.4 were measured.

TABLE 3

Chemical Constituent	Weight in grams
N-methyl-pyrrolidone	61.6 g
Cyclohexanone	102 g
Dispersylk-163	1.5 g (5% of the weight of pigment)
DARC polymer	52.4 g (22.9% in NMP only)
Pigment Black 26	30 g
DARC 100	60 g

Table 4 illustrates preferred composition with reference to Weight % for 2.4 optical density and 10^{11} ohm/square surface resistivity, at 1 micron film thickness.

TABLE 4

Chemical Composition	Weight %	Best Mode
Polyamic acid	4%-8%	5.7%
Colorant (dye + pigment)	9%-13%	11.5%
Dispersant	0.3%-0.8%	0.8%
Solvent	80%-85%	82.0%

EXAMPLE 2

In a plastic beaker is added 375 g of NMP, 375 g of cyclohexanone and 250 g of Pigment Black 26 (Daipyroxide TM Black 3551) with the primary particle size ranging from 10 to 20 nm and the surface of which is covered with thin silica layers. The mixture is stirred with a spatula for 5 minutes till homogeneous. This pigment slurry is then added to a ball mill together with quartz beads with 5 mm diameter of particle size, and ground at the speed of 100-200 rpm for 2 weeks. This mixture is dispersed at the speed of 7,000 rpm for 5 minutes in a homogenizer (Nihon Seiki Kaisha Ltd.) by adding 47.8 g of NMP and 21.0 g of cyclohexanone to it. In a separate glass beaker equipped with a mechanical stirrer is

added 67.4 g of DARC polymer (20 wt % in NMP only), 54.8 g of DARC 100, 69.8 g of NMP and 33.5 g of cyclohexanone. The mixture is dispersed in a homogenizer at the speed of 7,000 rpm for 5 minutes. In a homogenizer is added 225.3 g of the polymer/dye mixture and 175.7 g of the black pigment slurry. The homogenizer is then run at 10,000 rpm for 10 minutes. Formulation is then filtered through 0.2 µm filters. The formulation is summarized in Table 5.

TABLE 5

Chemical Composition	Weight %
Polyamic acid	4%-8%
Colorant	6%-10%
Dispersant	0.1%-0.4%
Solvent	85%-90%

(O.D. = 2.0 at 1 micron film thickness and surface resistivity of 3.3×10^{11} ohm/square)

Method of Use (Application)

Photolithography process is applied to get fine resolution and wide β-bake window. Prime substrate is cleaned. APX-K1, adhesion promoter from Shipley, is coated on substrate at 3000 rpm for 30 seconds, baked on hot plate at 175° C. for 30 seconds. Black matrix formulation is coated on APX-K1 coated substrate at 750 rpm for 90 seconds, α-baked to evaporate solvent on hot plate at 100° C. for 60 seconds. The coatings were then β-baked in conventional ovens at 120°-180° C. for 30 minutes. The polyamic acids is 30%-50% imidized in this process. Photoresist is coated at 5000 rpm for 30 seconds, soft baked on a hot plate at 100° C. for 30 seconds, exposed and developed. Photoresist is stripped in safestrip. Black matrix is then final cured in oven bake at 250° C. for 30 minutes which completes the imidization process. Other colors are applied and processed.

Characteristic Properties

FIG. 1 is a flow chart explaining the manufacturing process of a black matrix according to the present invention. FIG. 2 is a graph showing transmission spectra of 1 µm film obtained in Example 1. The material meets the goals of optical density and high resistivity. FIG. 3 shows sets of lithography data using both convection oven and hot plate beta-bake processes. Lithography results show a wide processing latitude. Resolution down to 3 µm at 1 µm film thickness are achievable within a wide range of intermediate (beta-bake) temperatures. FIG. 4 is a schematic diagram illustrating photo of a resolution dagger. FIG. 5 demonstrates Scanning Electron Microscope (SEM) of the black matrix material after resist removal and final cure. Good sidewall definition is evident in the pixel patterns. FIG. 6 is a schematic diagram illustrating typical surface roughness measurement of the cured film. Surface roughness measurements were taken on a lithography test sample in an area adjacent to a resolution dagger. The surface has a uniform microroughness that is well suited to a black matrix application. Resistivity measurements for a 1 µm film are on the order of 10^{11} Ω/square, thus providing a good balance of optical density and electrical properties. The composition can be applied by spin coating, imaged and developed using the same process used for RGB pixels. The average optical density for the 1 µm film thickness over the region 400-700 nm is 2.4. The material has good shelf life (3 months in freezer, 3 weeks at room temperature). It has low cost compared to chrome black matrix.

What is claimed:

1. A photolithographically imageable black matrix coating material having optical density ≥ 2.0 and surface resistivity greater than 10^3 ohm/square when coated at thicknesses ≤ 1.0 micron, consisting essentially of

- a. a polyimide precursor vehicle and a solvent system therefore.
- b. a soluble light-absorbing dye or mixtures of dyes, said dye or mixtures of dyes being substantially completely soluble in the vehicle and solvent system, and being effective to absorb substantially all light across a broad spectrum from ultra violet to infrared, and
- c. a mixed metal oxide non-carbon black pigment or mixture of pigments, and a dispersant therefor in Newtonian dispersion, said pigment or mixtures of pigments being substantially black in color.

2. The black matrix coating material of claim 1, wherein the polyimide vehicle solvent system is an effective mixture of NMP and cyclohexanone, the dye mixture is solvent brown 44 and solvent blue 67 at a weight/weight ratio of 1:3 to 1:5 and the pigment is a spinel structured oxide of metals and mixtures of multiple metals selected from the group consisting of copper, manganese, chromium, iron, magnesium, aluminum, zinc, tin, titanium, nickel, cobalt.

3. The black matrix coating material of claim 2 having a weight per cent composition of 4% to 8% polyimide vehicle, 80% to 85% solvent, 9% to 13% dye plus pigment wherein the weight/weight ratio of dye to pigment is 1:15 to 3:15, and the pigment is pigment black 26 made from a spinel structured oxide of metals and mixtures of multiple metals selected from copper, manganese and iron, having a C.I. of 77494, and 0.3% to 0.8% of a cationic dispersant made from high molecular weight blocked copolymers with chemical groups having strong affinity to the pigment black 26.

4. The coating material of claim 3 having a resistivity of at least 10^{11} ohm/square.

5. The black matrix coating material of claim 1 having a dye specified from color index of solvent black 3 to solvent black 47.

6. The coating material of claim 1 having a pigment specified from C.I. 77428 to 77494.

7. The coating material of claim 1 wherein the polyimide vehicle is selected from the group of reaction products of

- a. ODA and PMDA, and
- b. ODA and BTDA.

8. The coating material of claim 1 wherein the pigment dispersion comprises pigment particles having a particle size less than 100 nm.

9. The coating material of claim 1 wherein the surface of the pigments is coated with a material selected from the group consisting of silica, alumina and zirconia.

10. A method for making an organic black matrix coating material for STN or TFT pixel applications, said method comprising admixing

20 a. a polyimide precursor vehicle and light-absorbent organic broad spectrum light-absorbing dye capable of forming a high resistivity black coating and an effective solvent, and

25 b. a Newtonian dispersion of a black pigment having a C.I. from 77428 to 77494 at particle sizes less than 100 nm, and composed of mixed metal oxides of copper, manganese and iron, with an effective dispersant in the said effective solvent, and said dye and pigment being in a weight/weight ratio of about 1:15 to 3:15.

30 whereby the coating materials optical density is higher than 2.0 at ultra thin coating thicknesses without the need for admixing carbon black.

* * * * *



US005368976A

United States Patent [19]

Tajima et al.

[11] Patent Number: 5,368,976

[45] Date of Patent: Nov. 29, 1994

[54] PIGMENT-DISPersed COLOR-FILTER COMPOSITION comprising AN ALKALI-SOLUBLE BLOCK COPOLYMER AS A BINDER

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[73] Assignee: Japan Synthetic Rubber Co., Ltd., Tokyo, Japan

[21] Appl. No.: 36,253

[22] Filed: Mar. 24, 1993

[30] Foreign Application Priority Data

Mar. 27, 1992 [JP] Japan 4-100155
Jun. 11, 1992 [JP] Japan 4-151848
Jun. 24, 1992 [JP] Japan 4-166165

[51] Int. Cl^s G03F 7/016; G03F 7/008;
G03F 7/033

[52] U.S. Cl. 430/176; 430/7;
430/196; 430/197; 430/270; 430/281; 430/288;
430/910

[58] Field of Search 430/270, 196, 197, 281,
430/288, 7, 910, 176

[56]

References Cited

U.S. PATENT DOCUMENTS

4,460,675	7/1984	Gruetzmacher et al	430/283
4,614,701	9/1986	Mori et al	430/197
4,837,098	6/1989	Shinamura et al	430/7
4,902,726	2/1990	Hayashi et al	430/281
4,908,296	3/1990	Nebe et al	430/910
4,943,512	7/1990	Kawabata et al	430/197
5,047,309	9/1991	Koike et al	430/176
5,055,377	10/1991	Littmann et al	430/281
5,096,801	3/1992	Koya et al	430/293
5,110,710	5/1992	Tomita et al	430/281
5,190,845	3/1993	Hashimoto et al	430/288

FOREIGN PATENT DOCUMENTS

0076028	4/1983	European Pat. Off. .
0157374	10/1985	European Pat. Off. .
0480335	4/1992	European Pat. Off. .

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[57] ABSTRACT

The present invention provides a pigment dispersed color-filter composition containing a binder polymer such as an alkali-soluble block copolymer; a radiation-sensitive compound; and a pigment. The pigment-dispersed color-filter composition which further contains an organic medium, or an organic medium and a carboxylic acid is also provided.

6 Claims, No Drawings

**PIGMENT-DISPERSED COLOR-FILTER
COMPOSITION COMPRISING AN
ALKALI-SOLUBLE BLOCK COPOLYMER AS A
BINDER**

**DETAILED DESCRIPTION OF THE
INVENTION**

The present invention relates to a pigment-dispersed composition for a color-filter (to be referred to as "pigment-dispersed color-filter composition" hereinafter). More specifically, it relates to a pigment-dispersed color-filter composition useful for the production of color filters of a liquid crystal display and a charge coupled device.

For producing a color filter of a liquid display, a dyeing method, a printing method and an electrodeposition method are known. In recent years, a photolithographic method using a pigment-dispersed photosensitive composition is particularly attracting attention in terms of color purity, dimensional accuracy and process resistance ("Color Liquid Crystal Display" page 173, edited by Shunsuke Kobayashi, published by Sangyoto-sho, 1990).

However, the photolithographic method using a pigment-dispersed photosensitive composition having a variety of advantages is still required to have further improved performances for stably producing highly accurate and fine color filters. That is, a highly accurate and fine pixel is liable to peel off a substrate in a development step when a colored pixel of a color filter is formed by applying a pigment-dispersed photosensitive composition to the substrate, exposing the coating and developing it, and the color filter is thus liable to have a deficiency. On the other hand, when an attempt is made to improve the adhesion of a highly accurate and fine pixel to a substrate, the solubility of a non-pixel portion which should be dissolved away in a developer solution tends to decrease, and a so-called surface soiling and resin-remaining are liable to occur. In this case, it is general practice to apply a physical stimulus by rubbing the coating with a soft substance such as sponge or the like for removing the surface soiling and remaining resin. However, this practice is undesirable, since it involves toughening and occurrence of dust on the color filter surface, which ends up in a decrease in the yields of color filters.

When a color filter is produced from a radiation-sensitive composition, it is conventionally produced as follows. A light shielding layer in a desired pattern is formed on a glass substrate on which an SiO_2 film or the like has been formed to prevent the elution of sodium ion. A radiation-sensitive composition is spin-coated on the light shielding layer to form a coating, and the coating is heated (prebaked) and dried. The so-prepared dried coating (to be sometimes referred to as "dry coating" hereinafter) is exposed and developed to form a pixel of each color.

In the so-obtained dry coating formed on the substrate, the thickness of its central portion and the thickness of its marginal portion sometimes differs by $0.2 \mu\text{m}$ or more, and striation (streaks) sometimes occurs. It is therefore difficult to produce a dry coating having a uniform thickness. Further, an unevenness having a depth of approximately 300 to 500\AA is sometimes formed on the dry coating surface, and the dry coating surface is inferior in surface smoothness. When the surface of the coating formed by spin coating has a

nonuniform thickness or fine unevenness, a color filter obtained by developing the dry coating has inferior transparency.

For this reason, in forming a color filter on a substrate surface, it is therefore desired to develop a radiation-sensitive composition for a color filter, which is capable of forming a dry coating having a uniform thickness and having an excellently smooth surface.

When a conventional color filter is produced from a radiation-sensitive composition, a coating of the composition is developed with an alkaline aqueous solution. In this case, an undissolved substance from the radiation-sensitive composition sometimes remains on a non-pixel portion of the substrate. When an undissolved substance from the radiation-sensitive composition remains on the non-pixel portion of the substrate, the color filter shows a decline in transmittance or a decrease in contrast. When a color filter is produced, generally, pixels of three colors are consecutively produced by consecutively forming coatings of radiation-sensitive compositions each of which has a hue of red, blue or green. However, when an undissolved substance of the radiation-sensitive composition for forming a pixel of one of the colors remains on the substrate, a pixel of other color subsequently formed on the substrate where the undissolved substance remains is inferior in adhesion to the substrate and hence, it may peel off. The so-remaining undissolved radiation-sensitive composition on a non-pixel portion of the substrate surface is one of the reasons for decreasing the yields of color filters.

It is therefore an object of the present invention to provide a novel pigment-dispersed color-filter composition.

It is another object of the present invention to provide a novel pigment-dispersed color-filter composition which gives pixels having excellent adhesion to a substrate and is free of surface soiling and a remaining composition in development.

It is further another object of the present invention to provide a pigment-dispersed color-filter composition which gives a color filter having little difference in thickness between its central portion and its marginal portion and having excellent surface smoothness.

Further, it is another object of the present invention to provide a pigment-dispersed color-filter composition which is capable of uniformly forming pixels having excellent adhesion to a substrate without leaving an undissolved substance of the composition on a non-pixel portion when a color filter is produced.

It is still further another object of the present invention to provide a novel pigment-dispersed color-filter composition useful for producing a color filter for a liquid crystal display and a charge coupled device.

Other objects and advantages of the present invention will be apparent from the following description.

According to the present invention, the above objects and advantages of the present invention will be achieved, first, by a novel pigment-dispersed color-filter composition (to be referred to as "first composition" hereinafter) comprising:

- (A) an alkali-soluble block copolymer composed of a block having an acid group and a block having no acid group,
- (B) a radiation-sensitive compound, and
- (C) a pigment.

In the first composition of the present invention, an alkali-soluble block copolymer (A) composed of a block

having an acid group and a block having no acid group is used as a binder.

The block having an acid group is composed of a homopolymer formed from at least one monomer having an acid group such as an ethylenically unsaturated carboxylic acid and ethylenically unsaturated sulfonic acid, a copolymer of these or a copolymer formed from the above monomer having an acid group and a monomer having no acid group and being copolymerizable with the above monomer.

In view of ease in controlling the polymerization degree, preferred as the block having an acid group is a homopolymer of an ethylenically unsaturated carboxylic acid or a copolymer formed from an ethylenically unsaturated carboxylic acid and a monomer having no acid group and being copolymerizable therewith.

The ethylenically unsaturated carboxylic acid preferably includes acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, mono-methyl maleate and monomethyl fumarate.

The ethylenically unsaturated sulfonic acid includes isoprenesulfonic acid and styrenesulfonic acid.

The monomer having no acid group and being copolymerizable with the above monomer includes aromatic vinyl compounds such as styrene, α -methylstyrene and vinyltoluene; ethylenically unsaturated carboxylic acid esters such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate and benzyl (meth)acrylate; carboxylic acid vinyl esters such as vinyl acetate and vinyl propionate; vinyl cyanides such as (meth)acrylonitrile and α -chloroacrylonitrile; and aliphatic conjugated dienes such as 1,3-butadiene and isoprene.

The block having no acid group is formed of a polymer or copolymer composed from one of, or a plurality of, the above monomers such as aromatic vinyl compounds, ethylenically unsaturated alkyl carboxylic acid esters, vinyl carboxylic acid esters, vinyl cyanides and aliphatic conjugated dienes; ethylenically unsaturated carboxylic acid aminoalkyl esters such as aminoethyl acrylate; unsaturated aliphatic glycidyl esters such as glycidyl (meth)acrylate; macromonomers having a terminal (meth)acryloyl group such as polystyrene having a terminal (meth)acryloyl group; polymethyl (meth)acrylate having a terminal (meth)acryloyl group, polybutyl (meth)acrylate having a terminal (meth)acryloyl group and polysilicone having a terminal (meth)acryloyl group.

Of polymers or copolymers formed from the above monomers, preferred is a copolymer formed from a 50 macromonomer containing polystyrene, polymethyl (meth)acrylate, polybutyl (meth)acrylate or polysilicone.

The block copolymer can be produced by one of well known polymerization methods such as a living polymerization method, a method in which different blocks are bonded by a functional group reaction and a method using the macromonomer ["Kobunshi Gosei" (Polymer Synthesis), Essence of Polymer and Topics 2, Chapter 12, Junji Furukawa, published by Kagaku Dojin, 1986]. When the macromonomer is used, advantageously, the intended block copolymer can be obtained by a simple radical polymerization method.

When the block copolymer is produced, the amount of the monomer having an acid group is preferably 15 to 50% by weight based on the total amount of the monomers. When this amount is less than 15% by weight, the solubility of the block copolymer in an alkali developer

solution is insufficient, and a surface soiling and a resin-remaining are liable to occur on a non-pixel portion. When it exceeds 50% by weight, the solubility of the block copolymer in an alkali developer solution is too high, and pixels are liable to peel off a substrate. The amount of the monomer having an acid group is particularly preferably 20 to 40% by weight.

Concerning the molecular weight of the block copolymer, the weight average molecular weight of the 10 block copolymer as a polystyrene measured by gel permeation chromatography (to be abbreviated as GPC hereinafter) using tetrahydrofuran (THF) as a carrier is preferably 10,000 to 500,000, particularly preferably 20,000 to 300,000.

When the above molecular weight of the block copolymer exceeds 500,000, a scumming is liable to occur around developed pixels, a pattern edge is liable to show insufficient sharpness, and a surface soiling and resin-remaining are liable to occur on a non-pixel portion.

When the molecular weight of the block copolymer is less than 10,000, the solubility of the block copolymer in an alkali developer solution is too high under optimum development condition, and the time span for the development is small (for example about 20 to 40 seconds), and the so-called development time margin is liable to decrease.

The radiation-sensitive compound (B) can be selected, for example, from (1) a compound whose molecule is decomposed under irradiation with radiation to free an active compound, generate a chain reaction of unsaturated double bonds and form a three-dimensionally crosslinked compound and (2) a compound whose molecule is decomposed under irradiation with radiation to bond to a C—C bond or a C—H bond by an insertion reaction and form a three-dimensionally cross-linked structure.

The above (1) compound is selected from those compounds which generate radicals, carbene or nitrene, i.e., a photopolymerization initiator and a compound which has polyvalent unsaturated double bonds and is polymerized under irradiation with radiation, i.e., a photopolymerizable monomer and oligomer.

Examples of the photopolymerization initiator include a carbonium compound, an azo or azide compound, an organic sulfur compound, peroxide and a trihalomethane compound.

Specific examples of the carbonium compound include diacetyl, benzyl, benzoin, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 4-(2-hydroxyethoxy)phenyl-2-(hydroxy-2-propyl)ketone, 1-hydroxycyclohexylketone, 2,2-dimethoxy-2-phenylacetophenone, 2-methyl[4-(methylthio)phenyl]-2-morpholino-1-propan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholino-phenyl)-butan-1-one, benzophenone, 4,4'-bis(dimethylamino)benzophenone, 4,4'-bis(diethylamino)benzophenone, 2,4-diethylthioxanthone and 3,3-dimethyl-4-methoxybenzophenone.

Specific examples of the azo or azide compound include azoisobutyronitrile, diazonium, 4-azidobenzaldehyde, 4-azidoacetophenone, 4-azidobenzalacetophenone, 4-azidobenzalacetone, azidopyrene, 4-diazodiphenylamine, 4-diazo-4'-methoxydiphenylamine and 4-diazo-3'-methoxydiphenylamine.

Specific examples of the organic sulfur compound include mercaptan disulfide.

Specific examples of the peroxide include diethyl ether peroxide.

Specific examples of the trihalomethane include 1,3-bis(trichloromethyl)-5-(2'-chlorophenyl)-s-triazine and 1,3-bis(trichloromethyl)-5-(4'-methoxyphenyl)-s-triazine.

Examples of the photopolymerizable monomer or oligomer include polyacryloyl compounds such as trimethylopropane triacrylate, pentaerythritol triacrylate, trisacryloyloxyethyl phosphate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate and dipentaerythritol hexaacrylate; a condensate of 4-azidobenzaldehyde and polyvinyl alcohol, a condensate of 4-azidobenzaldehyde and a phenol novolak resin, and a polymer or copolymer of 4-acryloylphenylcinnamoyl ester.

The above (2) compound is selected from those compounds having at least two functional groups which generate carbene or nitrene under irradiation with radiation, i.e., photo-crosslinking agents.

Examples of the photo-crosslinking agents include diazidochalcone, 2,6-bis(4'-azidobenzal)cyclohexanone, 2,6-bis(4'-azidobenzal)-4-methylcyclohexanone, 1,3-bis(4'-azidobenzal)-2-propane, 1,3-bis(4'-azidocinnamylidene)-2-propanone, 4,4'-diazidostilbene and ammonium bichromate.

Of the above radiation-sensitive compounds, it is preferred to use a compound which generates radicals under irradiation with radiation as a photopolymerization initiator and a polyacryloyl compound as a photopolymerizable monomer or oligomer.

For example, 2-methyl[4-(methylthio)phenyl]-2-morpholino-1-propan-1-one or 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one is used as a photopolymerization initiator, and pentaerythritol triacrylate or dipentaerythritol hexaacrylate is used as a photopolymerizable monomer or oligomer. In this case, the amount of the photopolymerization initiator per 100 parts by weight of the photopolymerizable monomer or oligomer is 0.01 to 200 parts by weight, preferably 1 to 120 parts by weight.

The radiation-sensitive compound may be used in any amount as far as the first composition can form a coating having an adhesion under irradiation with radiation, and yet the amount of the radiation-sensitive compound per 100 parts by weight of the alkali-soluble block copolymer (A) is preferably 5 to 500 parts by weight, more preferably 20 to 200 parts by weight. When this amount is less than 5 parts by weight, the clearness of pixels is liable to be insufficient. When it exceeds 500 parts by weight, a resin is liable to remain on a non-pixel portion.

The pigment (C) is selected from both organic pigments and inorganic pigments.

As organic pigments, preferred are dyes and pigments which are insoluble in water or an organic solvent. Specific examples of the organic pigments are described in chapter "Pigment" under "Color Index" (published by The Society of Dyers and Colourists).

As inorganic pigments, preferred are metal-containing compounds such as metal oxides and metal complex salts. Specific examples of the inorganic pigments include oxides of iron, cobalt, aluminum, cadmium, lead, copper, titanium, magnesium, chromium, zinc and antimony and composite oxides of these.

Specifically, the pigment (C) includes the following.

- C. I. Pigment Yellow 24
- C. I. Pigment Yellow 31
- C. I. Pigment Yellow 53
- C. I. Pigment Yellow 83

- C. I. Pigment Orange 43
- C. I. Pigment Red 105
- C. I. Pigment Red 149
- C. I. Pigment Red 176
- C. I. Pigment Red 177
- C. I. Pigment Violet 14
- C. I. Pigment Violet 29
- C. I. Pigment Blue 15
- C. I. Pigment Blue 15:3
- C. I. Pigment Blue 22
- C. I. Pigment Blue 28
- C. I. Pigment Green 15
- C. I. Pigment Green 25
- C. I. Pigment Green 36
- C. I. Pigment Brown 28
- C. I. Pigment Black 1
- C. I. Pigment Black 7

The amount of the pigment (C) per 100 parts by weight of the alkali-soluble block copolymer (A) is 10 to 1,000 parts by weight, preferably 20 to 500 parts by weight. When this amount is less than 10 parts by weight, the color density in a pixel portion is liable to be insufficient. When it exceeds 1,000 parts by weight, a surface soiling and a resin-remaining are liable to occur on a non-pixel portion.

The first composition of the present invention may further contain other additives as required in addition to the above components (A), (B) and (C).

The above "other additives" include a filler, other polymer compound, a surfactant, an adhesion promoter, an antioxidant, an ultraviolet light absorber, an aggregation preventer and a sensitizer.

Specific examples of the other additives include fillers such as glass and alumina; polymer compounds such as polyvinyl alcohol, polyacrylic acid, polyethylene glycol monoalkyl ether and polyfluoroalkyl acrylate; non-ionic, cationic and anionic surfactants; adhesion promoters such as vinyltrimethoxysilane, vinyltriethoxysilane, vinyltris(2-methoxyethoxy)silane, N-(2-aminoethyl)3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)3-aminopropyltrimethoxysilane, 3-amino-propyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-chloropropylmethyldimethoxysilane, 3-chloropropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane; antioxidants such as 2,2-thiobis(4-methyl-6-t-butylphenol) and 2,6-di-t-butylphenol; ultraviolet light absorbers such as 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole and alkoxybenzophenone; aggregation preventers such as sodium polyacrylate and sodium polymethacrylate; and sensitizers such as benzophenone, 4,4'-bis(dimethylamino)benzophenone, 4,4'-bis(diethylamino)benzophenone and nitropyrene.

The solvent for dissolving the first composition of the present invention is preferably selected from alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol and i-propyl alcohol; cellosolves such as methyl cellosolve and ethyl cellosolve; carbitol type solvents such as diethylene glycol methyl ether and diethylene glycol ethyl ether; esters such as ethyl acetate, butyl acetate, methyl methoxypropionate, ethyl ethoxypropionate and ethyl lactate; ketones such as acetone, methyl isobutyl ketone and cyclohexanone; cellosolve acetates such as methylcellosolve acetate and ethylcellosolve acetate; carbitol acetate solvents such as diethylene glycol

methyl acetate and diethylene glycol ethyl acetate; ethers such as diethyl ether, ethylene glycol dimethyl ether, diethylene glycol diethyl ether (diglyme) and tetrahydrofuran; aprotic amide solvents such as N,N-dimethylformamide, N,N-dimethylacetamide and N-methylpyrrolidone; lactones such as T-butyrolactone, aromatic hydrocarbons such as benzene, toluene, xylene and naphthalene; and saturated hydrocarbons such as n-heptane, n-hexane and n-octane.

The first composition of the present invention can be prepared by mixing and dispersing the above components (A), (B) and (C) and optionally other additive(s) in the presence of the solvent by means of a ball mill, a pebble mill, a shaker, a homogenizer, a three-roll mill or a sand mill.

The substrate used for forming a color filter from the so-prepared first composition of the present invention includes soda glass, Pyrex glass, quartz glass and products prepared by forming a transparent electrically conductive coating on these glasses, which are used in a liquid crystal device, and a photoelectric transfer device substrate used in a solid camera device such as a silicon substrate.

According to the present invention, secondly, there is similarly provided a pigment-dispersed color-filter composition (to be referred to as "second composition" hereinafter) comprising:

- (A') a binder polymer,
- (B) a radiation-sensitive compound,
- (C) a pigment, and
- (D) a liquid medium containing at least 50% by weight of at least one organic medium which has a boiling point, measured at atmospheric pressure, of 100° to 200° C. and a vapor pressure, measured at 20° C., of 0.05 to 10 mmHg and is selected from the group consisting of an ester, an ether and a ketone.

The above second composition, when formed into a coating, gives a color filter having little difference in thickness between its central portion and its marginal portion and having excellent surface smoothness.

In the second composition, as the binder polymer (A'), preferred is a copolymer (e.g., random copolymer or block copolymer) obtained from an acid monomer (A'-1) and a comonomer (A'-2) copolymerizable with this acid monomer. The above acid monomer (A'-1) include unsaturated carboxylic acids having at least one carboxylic acid in the molecule such as unsaturated monocarboxylic acids and unsaturated dicarboxylic acids and unsaturated sulfonic acids having at least one sulfonic acid in the molecule. Specific examples of the unsaturated carboxylic acid include (meth)acrylic acid, crotonic acid, itaconic acid, maleic acid and fumaric acid.

Examples of the unsaturated sulfonic acids include isoprenesulfonic acid and styrenesulfonic acid.

The above acid monomers may be used alone or in combination.

Specific examples of the comonomer (A'-2) include aromatic vinyl compounds such as styrene, α -methylstyrene and vinyltoluene; unsaturated carboxylic acid alkyl esters such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate and benzyl (meth)acrylate; unsaturated carboxylic acid aminoalkyl esters such as aminoethyl acrylate; unsaturated carboxylic acid glycidyl esters such as glycidyl (meth)acrylate; carboxylic acid vinyl esters such as vinyl acetate and vinyl propionate; vinyl cyanide compounds such as (meth)acrylonitrile and α -

acrylonitrile; aliphatic conjugated dienes such as 1,3-butadiene and isoprene; and macromonomers such as polystyrene, polymethyl (meth)acrylate, polybutyl (meth)acrylate and polysilicone all of which have terminal (meth)acryloyl groups.

The above comonomers may be used alone or in combination.

When the binder polymer (A') is formed, the amount of the above acid monomer (A'-1) per 100% by weight of the total monomer amount is preferably 15 to 50% by weight, more preferably 20 to 40% by weight.

Specific examples of the above binder polymer (A') include a benzyl methacrylate/methacrylic acid/styrene copolymer, a methyl methacrylate/methacrylic acid/styrene copolymer, a benzyl methacrylate/methacrylic acid/polystyrene macromonomer copolymer and a methyl methacrylate/methacrylic acid/polystyrene macromonomer copolymer.

As the binder polymer (A'), preferred also is an alkali-soluble block copolymer composed of a block having an acid group and a block having no acid group. This alkali-soluble block copolymer includes those described regarding the first composition. For example, preferred is a block copolymer having, as a block having an acid group, a polymer selected from the group consisting of a homopolymer obtained from a monomer having an acid group, a copolymer obtained from monomers having acid groups and a copolymer obtained from a monomer having an acid group and a monomer having no acid group.

The binder polymer (A') having a structural unit derived from the above acid monomer (A'-1) exhibits solubility in an alkali.

The binder polymer (A') obtained from the acid monomer (A'-1) particularly in the above amount has excellent solubility in an alkali developer solution and forms almost no undissolved substance. Thus, almost no surface soiling or resin-remaining occurs on a non-pixel portion on a substrate. Further, the binder polymer (A') is not excessively dissolved in an alkali developer solution, and can serve to form color pixels which have excellent adhesion to a substrate and hardly peel off the substrate.

When measured by gel permeation chromatography (GPC, using THF as a carrier), the weight average molecular weight, as a polystyrene, of the binder polymer (A') used in the second composition is preferably 10,000 to 500,000, more preferably 20,000 to 300,000, particularly preferably 30,000 to 300,000.

The binder polymer (A') having the above molecular weight hardly causes a scumming (refuse on a surface) around color pixels in development, and can serve to form pixels having sharp pattern edges. Further, it hardly causes the remaining of a resin on a non-pixel portion on a substrate and hardly causes a surface soiling and resin-remaining. Further, the above binder polymer (A') serves to increase the development time during which the development can be carried out under optimum conditions, and thus increase the margin of development time.

In the second composition, the radiation-sensitive compound (B) can be selected from those described regarding the first composition.

In the second composition, the photopolymerization initiator, photopolymerizable monomer, photopolymerizable oligomer and photo-crosslinking agent, all of which are described regarding the first composition, may be used alone or in combination, and particularly,

it is preferred to use the photopolymerization initiator and either the photopolymerizable monomer or photopolymerizable oligomer in combination.

The amount of the radiation-sensitive compound (B) per 100 parts by weight of the binder polymer (A') is generally 5 to 500 parts by weight, preferably 20 to 200 parts by weight.

When the photopolymerization initiator and either the photopolymerizable monomer or photopolymerizable oligomer is used in combination, the amount of the photopolymerization initiator per 100 parts by weight of the photopolymerizable monomer or oligomer is 0.01 to 200 parts by weight, preferably 1 to 120 parts by weight.

Further, in the second composition, the pigment (C) can be selected from those described regarding the first composition.

In the second composition, the amount of the pigment (C) per 100 parts by weight of the binder polymer (A') is generally 10 to 1,000 parts by weight, preferably 20 to 500 parts by weight.

Further, the liquid medium (D) used in the second composition contains at least 50% by weight of an organic medium. The organic medium refers to an ester, an ether and a ketone which have a boiling point, measured at atmospheric pressure, of 100° to 200° C. and a vapor pressure, measured at 20° C., of 0.05 to 10 mmHg.

The above ester, ether and ketone specifically include the following:

Saturated aliphatic monocarboxylic acid alkyl esters such as n-butyl acetate and isobutyl acetate;

Lactic acid esters such as methyl lactate and ethyl lactate;

Oxyacetic acid alkyl esters such as methyl oxyacetate, ethyl oxyacetate and butyl oxyacetate;

Alkoxyacetic acid alkyl esters such as methyl methoxyacetate, ethyl methoxyacetate, butyl methoxyacetate, methyl ethoxyacetate and ethyl ethoxyacetate;

3-Oxypropionic acid alkyl esters such as methyl 3-oxypropionate and ethyl 3-oxypropionate;

3-Alkoxypropionic acid alkyl esters such as methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate and ethyl 3-ethoxypropionate;

2-Oxypropionic acid alkyl esters such as methyl 2-oxypropionate, ethyl 2-oxypropionate and propyl 2-oxypropionate;

2-Alkoxypropionic acid alkyl esters such as methyl 2-methoxypropionate, ethyl 2-methoxypropionate, propyl 2-methoxypropionate, methyl 2-ethoxypropionate and ethyl 2-ethoxypropionate;

2-Oxy-2-methylpropionic acid alkyl esters such as methyl 2-oxy-2-methylpropionate and ethyl 2-oxy-2-methylpropionate;

Monooxymonocarboxylic acid alkyl esters such as methyl 2-methoxy-2-methylpropionate and ethyl 2-ethoxy-2-methylpropionate;

Ketonic acid esters such as ethyl pyruvate;

Cellosolve acetates such as methylcellosolve acetate, ethylcellosolve acetate and diethylcellosolve acetate;

Ethers such as dichloroethyl ether, n-butyl ether, diisoamyl ether and methyl phenyl ether;

Carbitols such as methyl ethyl carbitol, diethyl carbitol, diethylene glycol methyl ethyl ether, diethylene glycol dimethyl ether and diethylene glycol diethyl ether;

Ketones such as cyclohexanone, methyl-n-propyl ketone, methyl-n-butyl ketone, methyl-n-amyl ketone and 2-heptanone.

The above organic media may be used alone or in combination.

The above ester, ether or ketone contained in the liquid medium (D) has a boiling point of 100° to 200° C. as described above, and preferred are organic media having a boiling point of 130° to 190° C.

10 The above ester, ether or ketone has a vapor pressure of 0.05 to 10.0 mmHg, and preferred are organic media having a vapor pressure of 0.1 to 5.0 mmHg.

Specific examples of the organic solvent preferably include ethyl lactate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, ethyl 2-ethoxypropionate, methylcellosolve acetate, ethylcellosolve acetate, diethylene glycol dimethyl ether, diethylene glycol diethyl ether and propylene glycol monomethyl ether acetate.

15 The liquid medium (D) contains at least 50% by weight, preferably at least 70% by weight, of at least one of the above ester, ether and ketone.

In addition to at least one of the above ester, ether and ketone, the liquid medium (D) contains other solvent, and this "other solvent" can be selected from any solvents which can disperse or dissolve the above pigment (C), the binder polymer (A') and the radiation-sensitive compound (B).

20 When the liquid medium (D) contains more than 50% by weight of a solvent whose boiling point is higher than 200° C., the liquid medium (D) is not sufficiently evaporated in prebaking a coating and remains in the dry coating. As a result, the dry coating surface may have the property of adhesion and cause sticking, and the heat resistance of the dry coating may decrease.

25 Further, when a large amount of the liquid medium (D) remains in the dry coating, the dry coating may peel off a glass substrate, particularly a glass substrate having an SiO₂ film on the surface, during the development.

30 On the other hand, when the liquid medium (D) contains more than 50% by weight of a solvent whose boiling point is lower than 100° C., it is difficult to apply the radiation-sensitive composition evenly and uniformly, and as a result, it is difficult to obtain a dry coating having excellent surface smoothness.

35 In the second composition, the amount of the liquid medium (D) per 100 parts by weight of the binder polymer (A') is generally 100 to 10,000 parts by weight, preferably 500 to 5,000 parts by weight.

40 The second composition of the present invention may contain other additives as required, such as a filler, other polymer compound, a surfactant, an adhesion promoter, an antioxidant, an ultraviolet absorber, an aggregation preventer and other sensitizer.

45 The above "other additives" include those described regarding the first composition.

50 The second composition of the present invention can be prepared by dissolving or dispersing the above components (A'), (B), (C) and (D) and optionally other component(s).

55 When the second composition is used, the organic solvent is sufficiently evaporated in a prebaking step, and there is no case where a large amount of the organic solvent remains in the dry coating. Therefore, the dry coating surface does not at all have the property of adhesion and does not cause sticking. Further, since no organic solvent remains in the dry coating in a large amount, the dry coating does not peel off the substrate, nor does the heat resistance decrease.

Further, the second composition can be evenly and uniformly applied onto a glass substrate with a spin coater. Therefore, the second composition can form a dry coating having a uniform thickness and having an excellently smooth surface without causing striation. Moreover, the so-formed dry coating has excellent adhesion to the substrate.

The above dry coating is developed with an alkali to give a color filter having excellent transparency.

When the second composition of the present invention is used, color filters having excellent transparency can be produced at high yields.

For forming pixels from the radiation-sensitive color-filter composition in the present invention, it is preferred to use an alkaline solution of at least one member selected from inorganic alkalis such as sodium carbonate, potassium hydroxide and potassium carbonate and organic alkalis such as tetramethylammonium hydroxide.

According to the present invention, thirdly, there is similarly provided a pigment-dispersed color-filter composition (to be referred to as "third composition" hereinafter) comprising:

- (A') a binder polymer,
- (B) a radiation-sensitive compound,
- (C) a pigment,
- (D) an organic medium, and
- (E) an organic carboxylic acid having a molecular weight of 1,000 or less and having at least one acid group in the molecule.

The above third composition is free of a remaining undissolved substance of this composition on a non-pixel portion on a substrate when a color filter is formed, and thus gives a color filter in which color pixels having excellent adhesion to a substrate are evenly and uniformly formed on the substrate.

In the third composition, the binder polymer (A'), the radiation-sensitive compound (B) and the pigment (C) can be selected from those described regarding the second composition.

It should be understood that the amounts of the radiation-sensitive compound (B) and the pigment (C) based on the binder polymer (A') are the same as those described regarding the second composition.

In the third composition, the organic medium (D) is selected from those described regarding the First composition.

Of those organic solvent, preferred are cellosolve acetates such as methoxyethyl acetate, ethoxyethyl acetate and ethylcellosolve acetate. carbitol acetate type solvents such as methoxyethoxyethyl acetate and ethoxyethoxyethyl acetate, ethers such as ethylene glycol dimethyl ether, diethylene glycol diethyl ether and propylene glycol diethyl ether and esters such as methyl methoxypropionate, ethyl ethoxypropionate and ethyl lactate.

In the third composition, the amount of the organic medium (D) per 100 parts by weight of the binder polymer (A') is 100 to 10,000 parts by weight, preferably 500 to 5,000 parts by weight.

The organic carboxylic acid (E) used in the third composition has a molecular weight of 1,000 or less and has at least one acid group in the molecule. Specifically, the organic carboxylic acid (E) is selected from aliphatic carboxylic acids and phenyl group-containing carboxylic acids.

Specific examples of the aliphatic carboxylic acids include monocarboxylic acids such as formic acid,

acetic acid, propionic acid, lactic acid, valeric acid, pivalic acid, caproic acid, diethylacetic acid, enanthic acid and caprylic acid; dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, brassylic acid, methylmalonic acid, ethylmalonic acid, dimethylmalonic acid, methylsuccinic acid, tetramethylsuccinic acid, cyclohexanedicarboxylic acid, itaconic acid, citraconic acid, maleic acid and fumaric acid; and tricarboxylic acids such as tricarballylic acid, aconitic acid and camphotonic acid.

Examples of the phenyl group-containing carboxylic acids include carboxylic acids in which a carboxyl group directly bonds to a phenyl group and carboxylic acids in which a carboxyl group is bond to a phenol group through a carbon bond.

Specific examples of the above phenyl group-containing carboxylic acids include monocarboxylic acids such as benzoic acid, toluic acid, cuminic acid, hemellitic acid and mesitylenic acid; polycarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, trimesic acid, mellophanic acid and pyromellitic acid; phenyl acetic acid, hydratropic acid, hydrocinnamic acid, mandelic acid, phenylsuccinic acid, atrophic acid, cinnamic acid, methyl cinnamate, benzyl cinnamate, cinnamylideneacetic acid, coumaric acid and unbellic acid.

Of the above acids, preferred are aliphatic or aromatic dicarboxylic acids such as malonic acid, citraconic acid, itaconic acid, mesaconic acid, fumaric acid and phthalic acid.

The above organic carboxylic acids may be used alone or in combination.

The content of the above organic carboxylic acid (E) in the third composition is preferably 0.001 to 10% by weight, more preferably 0.01 to 1% by weight.

When the content of the organic carboxylic acid (E) is less than 0.001% by weight, it may be impossible to prevent the remaining of an undissolved substance on a non-pixel portion on a substrate. When, it exceeds 10% by weight, the adhesion between pixels and the substrate may decrease.

The third composition of the present invention may further contain other additives as required. Examples of the "other additives" include a filler, other polymer compound, a surfactant, an adhesion promoter, an antioxidant, an ultraviolet light absorber and an aggregation preventer.

The above "other" additives can be specifically selected from those described regarding the first composition.

The third composition of the present invention is a radiation-sensitive composition for forming a color filter, and can form a color filter without causing a remaining of an undissolved substance on a non-pixel portion on a substrate surface in development.

The color-filter radiation-sensitive composition of the present invention is used for producing a color filter by forming a color pixel on a substrate, preferably on a substrate having a light-shielding layer pattern thereon, by a photolithographic method. When a pixel is formed from the color-filter radiation-sensitive composition of the present invention, no undissolved substance of the color-filter radiation-sensitive composition remains on a non-pixel portion, and the so-formed pixel, i.e., color filter is excellent in adhesion to the substrate or the light shielding layer pattern.

The pixel formed from the third composition of the present invention does not at all peel off a substrate. Further, the so-formed color filter is excellent in transmittance and contrast, and such color filters can be produced from the third composition of the present invention at high yields.

In the present invention, when pixels are formed from the color-filter radiation-sensitive composition, it is preferred to use an alkaline solution of sodium carbonate, sodium hydroxide, potassium hydroxide or tetramethylammonium hydroxide as a developer solution.

The present invention will be further detailed hereinafter by reference to Examples, in which "% stands for "% by weight" and "part" stands for "part by weight".

SYNTHESIS EXAMPLE 1

Ethylcellosolve acetate	100 parts
Methyl methacrylate	25 parts
Methacrylic acid	25 parts
Azoisobutyronitrile	1 part

The above materials were charged into an autoclave equipped with a stirrer, stirred at room temperature until a homogeneous mixture was formed, and its temperature was increased up to 80° C. Then, the mixture was kept at 80° C. for 3 hours, and then kept at 100° C. for 2 hours. The reaction mixture was cooled to room temperature to give a polymer solution A. During the above procedures, air was shut off the inside of the autoclave with nitrogen, and the mixture was continuously stirred. The yield of a polymer in the polymer solution A was 98%. The polymer (to be referred to as "polymer A" hereinafter, and to be similarly named hereinafter) in the polymer solution A had a weight average molecular weight as polystyrene (to be referred to as "weight average molecular weight" hereinafter) of 53,000 (measured by GPC using HLC-802A supplied by Toso Corp.)

Ethylcellosolve acetate	100 parts
Methyl methacrylate	30 parts
Styrene	18 parts
Glycidyl methacrylate	2 parts
Azoisobutyronitrile	2 parts

Separately, the above materials were charged into an autoclave equipped with a stirrer, and a polymer solution B was obtained in the same manner as in the procedures for obtaining the polymer solution A. The yield of a polymer in the polymer solution B was 99% or more. The polymer B has a weight average molecular weight of 62,000.

Then, the polymer solution A and the polymer solution B in equal amounts were mixed and kept at 100° C. for 12 hours with stirring to promote a reaction between carboxyl group of the polymer A and glycidyl group of the polymer B, whereby a polymer solution C was obtained. The polymer C had a weight average molecular weight of 140,000.

SYNTHESIS EXAMPLE 2

Diglyme	200 parts
Benzyl acrylate	50 parts
Methacrylic acid	30 parts
Macromonomer AS-6 ¹	20 parts

-continued

Azoisobutyronitrile	1 part
(1: Polystyrene terminated with methacryloyl, average molecular weight 6,000, supplied by Toagosei Chemical Industries Co., Inc.)	

The above materials were charged into an autoclave equipped with a stirrer, stirred at room temperature until a homogeneous mixture was formed and then, the temperature was raised up to 80° C. Then, the mixture was kept at 80° C. for 3 hours, and then kept at 100° C. for 2 hours. The reaction mixture was cooled to room temperature to give a polymer solution D. During the above procedures, air was shut off the autoclave interior with nitrogen, and the mixture was continuously stirred. The yield of a polymer in the polymer solution D was 98%. The polymer D had a weight average molecular weight of 65,000.

SYNTHESIS EXAMPLE 3

20 A polymer solution E was obtained in the same manner as in Synthesis Example 2 except that the temperature of 80° C. for keeping the mixture was changed to 70° C. The yield of a polymer in the polymer solution E was 98%. The polymer E had a weight average molecular weight of 120,000.

SYNTHESIS EXAMPLE 4

30 A polymer solution F was obtained in the same manner as in Synthesis Example 2 except that the temperature of 80° C. for keeping the mixture was changed to 60° C. The yield of a polymer in the polymer solution F was 98%. The polymer F had a weight average molecular weight of 270,000.

SYNTHESIS EXAMPLE 5

35 A polymer solution G was obtained in the same manner as in Synthesis Example 2 except that the amount of azoisobutyronitrile was changed to 3 parts and that the temperature of 80° C. for keeping the mixture was changed to 90° C. The yield of a polymer in the polymer solution G was 99%. The polymer G had a weight average molecular weight of 28,000.

SYNTHESIS EXAMPLE 6

Toluene	1,000 parts
Methyl methacrylate	75 parts
Styrene	25 parts
m-Butyllithium	1 part

55 A methyl methacrylate/styrene block copolymer was synthesized by the use of the above materials according to a method described in a piece of literature (C. W. Brown & I. F. White, J. Appl. Polym. Sci., 16, 2671-2676, 1972), and then the ester group was hydrolyzed. The hydrolysis was controlled by adjusting the time for hydrolysis treatment, and as a result, a polymer H whose hydrolysis ratio was 38% was obtained. The 60 polymer H had a weight average molecular weight of 130,000. 100 Parts of the polymer H was dissolved in 200 parts of ethylcellosolve to obtain a polymer solution H.

SYNTHESIS EXAMPLE 7

A polymer solution I was obtained in the same manner as in Synthesis Example 2 except that 10 parts of methacrylic acid out of 30 parts of methacrylic acid was

replaced with 10 parts of styrenesulfonic acid. The yield of a polymer in the polymer solution I was 97. The polymer I had a weight average molecular weight of 53,000.

EXAMPLE 1

C. I. Pigment Blue 15	15 parts
Pentaerythritol triacrylate	20 parts
Irgacure 184 ^{*2}	3 parts
<u>Polymer solution C obtained in Synthesis</u>	
Example 1	60 parts
Bm-1000 ^{*3}	2 parts
Vinylimethoxysilane	3 parts
Ethylcellosolve acetate	300 parts

(*2: 1-hydroxycyclohexyl phenyl ketone, supplied by Ciba Geigy.)
(*3: fluorine-containing nonionic surfactant, supplied by BM Chemie.)

The above materials were placed in a ball mill with 3 mmΦ steel balls in it, and mixed and dispersed for 18 hours.

The resultant dispersion was filtered through a filter having a pore diameter of 10 µm to give a dispersion of a composition of the present invention.

When the dispersion of the composition was stored in a dark place at room temperature for 1 week, no pigment precipitated, no polymer precipitated, and there was no change in viscosity. The dispersion remained uniform.

The above dispersion was coated on a glass substrate with a spin coater to form a dry coating having a thickness of 2 µm, and dried at 80° C. for 15 minutes to give a blue uniform coating. The so-formed coating was free of defects such as voids and roughened surface.

Further, the coating was exposed to a high-pressure mercury lamp at a light energy of 300 mJ/cm² through a photomask having a mask opening breadth of 10 to 100 µm for resolution evaluation, and developed with an aqueous solution containing 0.1% of tetramethylammonium hydroxide. The coating was rinsed with water and dried at 180° C. for 60 minutes.

The so-obtained pixel had a pattern formed of fine lines having a breadth of 10 to 100 µm, and was free of coating defects such as pinholes and toughened coating. When observed through a microscope, it was found that there was no nonuniform breadth of lines of the pattern and that the line edges were sharp. Further, neither the pigment nor the organic coating remained on a non-pixel portion, and the pixel was suitable as a color filter. Table 1 shows the evaluation results.

EXAMPLE 2

A dispersion of a composition was obtained in the same manner as in Example 1 except that the polymer solution C was replaced with the polymer solution D obtained in Synthesis Example 2. Table 1 shows the evaluation results.

EXAMPLE 3

A dispersion of a composition was obtained in the same manner as in Example 1 except that the polymer solution C was replaced with the polymer solution E obtained in Synthesis Example 3. Table 1 shows the evaluation results.

EXAMPLE 4

A dispersion of a composition was obtained in the same manner as in Example 1 except that the polymer solution C was replaced with the polymer solution F obtained in Synthesis Example 4. Table 1 shows the evaluation results.

EXAMPLE 5

10 A dispersion of a composition was obtained in the same manner as in Example 1 except that the polymer solution C was replaced with the polymer solution G obtained in Synthesis Example 5. Table 1 shows the evaluation results.

EXAMPLE 6

A dispersion of a composition was obtained in the same manner as in Example 1 except that the polymer solution C was replaced with the polymer solution H obtained in Synthesis Example 6. Table 1 shows the evaluation results.

EXAMPLE 7

25 A dispersion of a composition was obtained in the same manner as in Example 1 except that the polymer solution C was replaced with the polymer solution I obtained in Synthesis Example 7. Table 1 shows the evaluation results.

EXAMPLE 8

A dispersion of a pigment was obtained in the same manner as in Example 2 except that the C. I. Pigment Blue 15 was replaced with C. I. Pigment Red 177. Table 35 shows the evaluation results.

EXAMPLE 9

A dispersion of a pigment was obtained in the same manner as in Example 2 except that the C. I. Pigment Blue 15 was replaced with C. I. Pigment Green 36. Table 35 shows the evaluation results.

COMPARATIVE SYNTHESIS EXAMPLE 1

All the materials used in Synthesis Example 1, i.e.,

Ethylcellosolve acetate	200 parts
Methyl methacrylate	55 parts
Methacrylic acid	25 parts
Styrene	18 parts
Glycidyl methacrylate	2 parts
Azoisobutyronitrile	3 parts

were charged into an autoclave equipped with a stirrer, stirred at room temperature until a uniform mixture was formed and thereafter, the temperature was increased up to 80° C. Then, the mixture was kept at 80° C. for 3 hours, and then kept at 100° C. for 2 hours. The reaction mixture was cooled to room temperature to give a polymer solution α. The yield of a polymer in the polymer solution was 99% or more. The polymer α had a weight average molecular weight of 92,000.

COMPARATIVE EXAMPLE 1

A dispersion of a composition was obtained in the same manner as in Example 1 except that the polymer solution C was replaced with the polymer solution α obtained in Comparative Synthesis Example 1.

TABLE 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Comp. Ex. 1
Clearness in pixel portion ^{a4}	◎	◎	◎	○	○	○	○	○	○	△
Pixel peeling in development	◎	○	○	○	○	○	○	○	○	
Surface soiling on non-pixel portion	○	○	○	○	○	○	○	○	○	X
Margin of development time ^{a5}	○	○	○	○	○	○	○	○	○	

◎ Excellent

○ Good

△ Poor

X Defective

^{a4}: A linear pixel having a line breadth of 10 μm was formed and at the same time it had a clear outline.

^{a5}: A development time of at least 30 seconds was available for providing an optimum development state.

TABLE 3

15	Compound	part
Pigment	C.I. Pigment Red 177	90
Binder	Benzyl methacrylate/methacrylic acid/styrene copolymer (compositional weight ratio 65/25/10, weight average molecular weight 40,000)	50
Radiation-sensitive compound	Trimethylolpropane triacrylate (M-309, supplied by Toagosei Chemical Industries Co., Inc.)	40
	1-Hydroxycyclohexyl phenyl ketone (I-184, supplied by Japan Ciba Geigy)	24
Organic solvent	Diethylene glycol monoethyl ether	796

EXAMPLE 10

A light shielding layer having a desired form was formed on a soda glass substrate surface on which an SiO₂ film had been formed for preventing sodium ion elution. Then, a color-filter radiation-sensitive composition shown in Table 2 was coated on the light shielding layer with a spin coater to form a desired coating thickness of 1.5 μm, and the so-formed coating was prebaked at 80° C. for 10 minutes to obtain a dry coating.

TABLE 2

	Compound	part
Pigment	C.I. Pigment Red 177	90
Binder	Benzyl methacrylate/methacrylic acid/styrene copolymer (compositional weight ratio 65/25/10, weight average molecular weight 40,000)	50
Radiation-sensitive compound	Trimethylolpropane triacrylate (M-309, supplied by Toagosei Chemical Industries Co., Inc.)	40
	1-Hydroxycyclohexyl phenyl ketone (I-184, supplied by Japan Ciba Geigy)	24
Organic solvent	Ethyl 3-ethoxypropionate (boiling point; 170.1° C., vapor pressure; 1.5 mmHg)	796

The above-obtained dry coating was measured with a tracer-method film thickness measuring apparatus (al-ph-step 100, supplied by TENCOR) to show the following. The coating thickness was 1.45 to 1.50 μm, or the in-plane thickness variation of the coating (in-plane thickness difference) was 0.05 μm or less, and the coating surface roughness (unevenness) was about 100Å. The dry coating was excellent in transparency. Further, the dry coating had no striation.

Then, the dry coating was exposed to ultraviolet light at 400 mJ/cm² from a high pressure mercury lamp through a photomask, and developed by immersing the dry coating in an aqueous solution containing 0.05% of sodium carbonate to give red pixels having a size of 100 μm × 100 μm each.

The so-formed color pixels were observed through a differential polarization microscope to show high surface smoothness and hence, they were desirable for a color filter.

COMPARATIVE EXAMPLE 2

A dry coating was formed in the same manner as in Example 10 except that the organic solvent was replaced with diethylene glycol monoethyl ether (boiling point 202° C., vapor pressure 0.13 mmHg). That is, the radiation-sensitive composition shown in Table 3 was used.

The dry coating was measured in the same manner as in Example 10 to show the following. The coating thickness was 1.42 to 1.60 μm, or the in-plane thickness variation of the coating was 0.18 μm, and the coating surface roughness (unevenness) was about 500Å. The dry coating was not transparent.

The dry coating was also exposed in the same manner as in Example 10 to obtain red pixels having a size of 100 μm × 100 μm each.

The so-formed color pixels were observed through a differential polarization microscope to show that they did not have high surface smoothness and hence, they were undesirable for a color filter.

COMPARATIVE EXAMPLE 3

A dry coating was formed in the same manner as in Example 10 except that the organic solvent was replaced with methyl ethyl ketone (boiling point 79.6° C., vapor pressure 71.2 mmHg). That is, the radiation-sensitive composition shown in Table 4 was used.

TABLE 4

50	Compound	part
Pigment	C.I. Pigment Red 177	90
Binder	Benzyl methacrylate/methacrylic acid/styrene copolymer (compositional weight ratio 65/25/10, weight average molecular weight 40,000)	50
Radiation-sensitive compound	Trimethylolpropane triacrylate (M-309, supplied by Toagosei Chemical Industries Co., Inc.)	40
	1-Hydroxycyclohexyl phenyl ketone (I-184, supplied by Japan Ciba Geigy)	24
Organic solvent	Methyl ethyl ketone	796

The dry coating was measured in the same manner as in Example 10 to show the following. The coating thickness was 1.26 to 1.61 μm, or the in-plane thickness variation of the coating was 0.35 μm, and the coating surface roughness (unevenness) was about 600Å.

The dry coating was not transparent. Further, the dry coating had striation.

The dry coating was also exposed in the same manner as in Example 10 to obtain red pixels having a size of 100 $\mu\text{m} \times 100 \mu\text{m}$ each.

The so-formed color pixels were observed through a differential polarization microscope to show that they did not have high surface smoothness and hence, they were undesirable for a color filter.

EXAMPLE 11

A dry coating was formed in the same manner as in Example 10 except that the organic solvent was replaced with propylene glycol monomethyl ether (boiling point 140° C., vapor pressure 3.5 mmHg). That is, the radiation-sensitive composition shown in Table 5 was used.

TABLE 5

	Compound	part
Pigment	C.I. Pigment Blue 15	90
Binder	Benzyl methacrylate/methacrylic acid/styrene copolymer (compositional weight ratio 65/25/10, weight average molecular weight 40,000)	50
Radiation-sensitive compound	Trimethylolpropane triacrylate (M-309, supplied by Toagosei Chemical Industries Co., Inc.)	40
Organic solvent	1-Hydroxycyclohexyl phenyl ketone (I-184, supplied by Japan Ciba Geigy) Propylene glycol monomethyl ether acetate	24 796

The dry coating was measured in the same manner as in Example 10 to show the following. The coating thickness was 1.50 to 1.59 μm , or the in-plane thickness variation of the coating was 0.09 μm or less, and the coating surface roughness (unevenness) was about 200 Å.

The dry coating was excellent in transparency, and had no striation.

Then, the dry coating was also exposed in the same manner as in Example 10 to obtain blue pixels having a size of 100 $\mu\text{m} \times 100 \mu\text{m}$ each.

The so-formed color pixels were observed through a differential polarization microscope to show that they had high surface smoothness and hence, they were desirable for a color filter.

EXAMPLE 12

A dry coating was obtained in the same manner as in Example 10 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 6.

TABLE 6

	Compound	part
Pigment	C.I. Pigment Red 177	90
Binder	Benzyl methacrylate/methacrylic acid/styrene copolymer (compositional weight ratio 65/25/10, weight average molecular weight 40,000)	50
Radiation-sensitive compound	Dipentaerythritol pentaacrylate (M-400, supplied by Toagosei Chemical Industries Co., Inc.)	40
Organic solvent	2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (I-369, supplied by Japan Ciba Geigy) Diethylene glycol dimethyl ether (boiling point; 159.8° C., vapor pressure 3.4 mmHg) Carbitol acetate (boiling point; 217.4° C., vapor pressure 0.1 mmHg)	24 710 86

The dry coating was measured in the same manner as in Example 10 to show the following. The coating thickness was 1.50 to 1.59 μm , or the in-plane thickness variation of the coating was 0.09 μm or less, and the coating surface roughness (unevenness) was about 200 Å.

The dry coating was excellent in transparency, and had no striation.

Then, the dry coating was also exposed in the same manner as in Example 10 to obtain red pixels having a size of 100 $\mu\text{m} \times 100 \mu\text{m}$ each.

The so-formed color pixels were observed through a differential polarization microscope to show that they had high surface smoothness and hence, they were desirable for a color filter.

COMPARATIVE EXAMPLE 4

A dry coating was obtained in the same manner as in Example 10 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 7.

TABLE 7

	Compound	part
25	Pigment C.I. Pigment Green 7	90
	Benzyl methacrylate/methacrylic acid/poly-styrene macromonomer copolymer (polystyrene macromonomer: AS-6, supplied by Toagosei Chemical Industries Co., Ltd.) (compositional weight ratio 65/25/10, weight average molecular weight 40,000)	50
Radiation-sensitive compound	Trimethylolpropane triacrylate (Biscoat 295, supplied by Osaka Organic Chemical Industry Ltd.)	40
35	2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (I-369, supplied by Japan Ciba Geigy)	24
Organic solvent	Diethylene glycol dimethyl ether (boiling point; 159.8° C., vapor pressure 3.4 mmHg) n-butyl carbitol acetate (boiling point; 246.8° C., vapor pressure 0.1 mmHg or less)	316 474

The dry coating obtained in the same manner as in Example 10 was not fully dried when prebaked at 80° C. for 10 minutes, and tackiness (stickiness on coating surface) was observed. Therefore, the coating was prebaked at 90° C. for 10 minutes to obtain a dry coating. The coating thickness was 1.32 to 1.50 μm , or the in-plane thickness variation of the coating was 0.18 μm or less, and the coating surface roughness (unevenness) was about 400 Å.

The coating was not transparent, and had striation.

The dry coating was exposed in the same manner as in Example 10 to obtain green pixels having a size of 100 $\mu\text{m} \times 100 \mu\text{m}$ each.

The so-formed pixels were observed through a differential polarization microscope to show that they did not have high surface smoothness and hence, they were undesirable for a color filter.

EXAMPLE 13

A dry coating was obtained in the same manner as in Example 10 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 8.

TABLE 8

	Compound	part
Pigment	C.I. Pigment Green 7	90

TABLE 8-continued

	Compound	part
Binder	Benzyl methacrylate/methacrylic acid/styrene macromonomer copolymer (polystyrene macromonomer: AS-6, supplied by Toagosei Chemical Industries Co., Ltd.) (compositional weight ratio 65/25/10, weight average molecular weight 40,000)	50
Radiation-sensitive compound	Trimethylolpropane triacrylate (Biscoat 295, supplied by Osaka Organic Chemical Industry Ltd)	40
Organic solvent	2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (I-369, supplied by Japan Ciba Geigy) Diethylene glycol dimethyl ether (boiling point; 159.8°C, vapor pressure 3.4 mmHg) n-Butylcarbitol acetate (boiling point; 246.8°C, vapor pressure 0.1 mmHg or less)	24 570 220

The dry coating was measured in the same manner as in Example 10 to show the following. The coating thickness was 1.47 to 1.53 µm, or the in-plane thickness variation of the coating was 0.06 µm or less, and the coating surface roughness (unevenness) was about 200Å.

The dry coating was excellent in transparency, and had no striation.

Then, the dry coating was also exposed in the same manner as in Example 10 to obtain green pixels having a size of 100 µm × 100 µm each.

The so-formed color pixels were observed through a differential polarization microscope to show that they had high surface smoothness and hence, they were desirable for a color filter.

EXAMPLE 14

A dry coating was obtained in the same manner as in Example 10 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 9.

TABLE 9

	Compound	part
Pigment	C.I. Pigment Green 7	90
Binder	Benzyl methacrylate/methacrylic acid/styrene macromonomer copolymer (polystyrene macromonomer: AS-6, supplied by Toagosei Chemical Industries Co., Ltd.) (compositional weight ratio 65/25/10, weight average molecular weight 40,000)	50
Radiation-sensitive compound	Trimethylolpropane triacrylate (Biscoat 295, supplied by Osaka Organic Chemical Industry Ltd)	40
Organic solvent	2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (I-369, supplied by Japan Ciba Geigy) Diethylene glycol dimethyl ether (boiling point; 159.8°C, vapor pressure 3.4 mmHg) Methyl ethyl ketone (boiling point; 79.6°C, vapor pressure 71.2 mmHg)	24 570 220

The dry coating was measured in the same manner as in Example 10 to show the following. The coating thickness was 1.62 to 1.69 µm, or the in-plane thickness variation of the coating was 0.10 µm or less, and the coating surface roughness (unevenness) was about 200Å.

The dry coating was excellent in transparency, and had no striation.

Then, the dry coating was also exposed in the same manner as in Example 10 to obtain green pixels having a size of 100 µm × 100 µm each.

The so-formed color pixels were observed through a differential polarization microscope to show that they had high surface smoothness and hence, they were desirable for a color filter.

COMPARATIVE EXAMPLE 5

10 A dry coating was obtained in the same manner as in Example 10 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 10.

TABLE 10

	Compound	part
Pigment	C.I. Pigment Green 7	90
Binder	Benzyl methacrylate/methacrylic acid/styrene macromonomer copolymer (polystyrene macromonomer: AS-6, supplied by Toagosei Chemical Industries Co., Ltd.) (compositional weight ratio 65/25/10, weight average molecular weight 40,000)	50
Radiation-sensitive compound	Trimethylolpropane triacrylate (Biscoat 295, supplied by Osaka Organic Chemical Industry Ltd)	40
Organic solvent	2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (I-369, supplied by Japan Ciba Geigy) Diethylene glycol dimethyl ether (boiling point; 159.8°C, vapor pressure 3.4 mmHg) Methyl ethyl ketone (boiling point; 79.6°C, vapor pressure 71.2 mmHg)	24 316 474

The dry coating was measured in the same manner as in Example 10 to show the following. The coating thickness was 1.68 to 1.98 µm, or the in-plane thickness variation of the coating was 0.30 µm, and the coating surface roughness (unevenness) was about 400Å.

The coating was not transparent, and had striation.

40 The dry coating was exposed in the same manner as in Example 10 to obtain green pixels having a size of 100 µm × 100 µm each.

The so-formed pixels were observed through a differential polarization microscope to show that they did not have high surface smoothness and hence, they were undesirable for a color filter.

EXAMPLE 15

A light shielding layer having a desired form was formed on a soda glass substrate surface on which an SiO₂ film had been formed for preventing sodium ion elution. Then, a color-filter radiation-sensitive composition shown in Table 11 was coated on the light shielding layer with a spin coater to form a desired coating thickness, and the so-formed coating was dried at 80°C for 10 minutes, and then cooled. Then, the so-formed color filter layer was exposed to ultraviolet light at 400 mJ/cm² from a high pressure mercury lamp through a photomask, and developed by immersing the substrate in an aqueous solution containing 0.05% of sodium carbonate to give red pixels having a size of 20 µm × 20 µm each.

TABLE 11

	Compound	part
Pigment	C.I. Pigment Red 177	90
Binder	Benzyl methacrylate/methacrylic acid/styrene copolymer (compositional weight ratio 65/25/10, average molecular weight Mw	50

TABLE 11-continued

	Compound	part
Radiation-sensitive compound	40,000) Trimethylolpropane triacrylate (M-309, supplied by Toagosei Chemical Industries Co., Inc.)	40
Solvent	1-Hydroxycyclohexyl phenyl ketone (I-184, supplied by Japan Ciba Geigy)	24
Organic acid	Ethylcellosolve acetate	790
	Oxalic acid	6

The so-formed color pixels gave a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

The same color-filter radiation-sensitive composition as the above color-filter radiation-sensitive composition was allowed to stand at room temperature for 3 days, and then red pixels were formed in the same manner as above and developed by immersing the substrate in an aqueous solution containing 0.05% of sodium carbonate to give a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

COMPARATIVE EXAMPLE 6

Red pixels were formed in the same manner as in Example 15 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 12.

TABLE 12

	Compound	part
Pigment	C.I. Pigment Red 177	90
Binder	Benzyl methacrylate/methacrylic acid/styrene copolymer (compositional weight ratio 65/25/10, average molecular weight Mw 40,000)	50
Radiation-sensitive compound	Trimethylolpropane triacrylate (M-309, supplied by Toagosei Chemical Industries Co., Inc.)	40
Solvent	1-Hydroxycyclohexyl phenyl ketone (I-184, supplied by Japan Ciba Geigy)	20
	Ethylcellosolve acetate	796

In the above-formed color pixels, an undissolved substance was formed in a non-pixel portion on the substrate.

When the concentration of sodium carbonate was increased to 0.5% the undissolved portion decreased in amount, but the formed pixels partly peeled off and the sharpness of the pixel edges declined.

EXAMPLE 16

Blue pixels were formed in the same manner as in Example 15 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 13.

TABLE 13

	Compound	part
Pigment	C.I. Pigment Blue 15	90
Binder	Benzyl methacrylate/methacrylic acid/styrene copolymer (compositional weight ratio 65/25/10, average molecular weight Mw 40,000)	50
Radiation-sensitive compound	Dipentaerythritol pentaacrylate (M-400, supplied by Toagosei Chemical Industries Co., Inc.)	40
Solvent	2,2-Dimethoxy-2-phenylacetophenone (I-651 supplied by Japan Ciba Geigy)	20
Organic acid	Diethylene glycol dimethyl ether	790
	Itaconic acid	6

TABLE 13-continued

	Compound	part
5	carboxylic acid	

The above-formed color pixels gave a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

Further, after the same color-filter radiation-sensitive composition as the above color-filter radiation-sensitive composition was allowed to stand at room temperature for 3 days in the same manner as in Example 15, it gave a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

COMPARATIVE EXAMPLE 7

An attempt was made to form blue pixels in the same manner as in Example 15 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 14.

TABLE 14

	Compound	part
25	Pigment	C.I. Pigment Blue 15
	Binder	Benzyl methacrylate/methacrylic acid/styrene copolymer (compositional weight ratio 65/25/10, average molecular weight Mw 40,000)
30	Radiation-sensitive compound	Dipentaerythritol pentaacrylate (M-400, supplied by Toagosei Chemical Industries Co., Inc.)
		2,2-Dimethoxy-2-phenylacetophenone (I-651 supplied by Japan Ciba Geigy)
35	Solvent	Diethylene glycol dimethyl ether
	Organic carboxylic acid	Itaconic acid

The above color-filter radiation-sensitive composition contained a large amount, as large as 15% by weight, of itaconic acid (organic carboxylic acid). Therefore, when a dry coating was developed with a sodium carbonate aqueous solution, both the pixel portion and the non-pixel portion were dissolved away in the sodium carbonate aqueous solution, and no pixels were formed.

Even when the concentration of sodium carbonate in an aqueous solution was decreased to 0.001%, there was no change in the result.

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EXAMPLE 17

Green pixels were formed in the same manner as in Example 15 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 15.

TABLE 15

	Compound	part
60	Pigment	C.I. Pigment Green 7
	Binder	Benzyl methacrylate/methacrylic acid/styrene copolymer (compositional weight ratio 65/25/10, average molecular weight Mw 40,000)
65	Radiation-sensitive compound	Trimethylolpropane triacrylate (Biscoat 295, supplied by Osaka Organic Chemical Industry Ltd.)
		2,2-Dimethoxy-2-phenylacetophenone (I-651 supplied by Japan Ciba Geigy)
70	Solvent	Diethylene glycol dimethyl ether
	Organic acid	Phthalic acid

TABLE 15-continued

Compound	part
carboxylic acid	

The above-formed color pixels gave a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

Further, after the same color-filter radiation-sensitive composition as the above color-filter radiation-sensitive composition was allowed to stand at room temperature for 3 days in the same manner as in Example 15, it gave a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

EXAMPLE 18

Red pixels were formed in the same manner as in Example 15 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 16.

TABLE 16

Compound	part
Pigment C.I. Pigment Red 177	90
Binder Methacrylate/methacrylic acid/styrene copolymer (compositional weight ratio 65/25/10, average molecular weight Mw 40,000)	50
Radiation-sensitive compound Trimethylolpropane triacrylate (M-309, supplied by Toagosei Chemical Industries Co., Inc.)	40
Solvent Organic carboxylic acid 1-Hydroxycyclohexyl phenyl ketone (I-184 supplied by Japan Ciba Geigy)	24
Organic carboxylic acid Ethylcellosolve acetate	790
Malonic acid	6

The above-formed color pixels gave a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

Further, after the same color-filter radiation-sensitive composition as the above color-filter radiation-sensitive composition was allowed to stand at room temperature for 3 days in the same manner as in Example 15, it gave a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

EXAMPLE 19

Green pixels were formed in the same manner as in Example 15 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 17.

TABLE 17

Compound	part
Pigment C.I. Pigment Green 7	90
Binder Benzyl methacrylate/methacrylic acid/poly-styrene macromonomer (compositional weight ratio 65/25/10, average molecular weight Mw 40,000)	50
Radiation-sensitive compound Trimethylolpropane triacrylate (Biscoat 295, supplied by Osaka Organic Chemical Industry Ltd)	40
Solvent Organic carboxylic acid 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (I-369 supplied by Japan Ciba Geigy)	24
Organic carboxylic acid Diethylene glycol dimethyl ether	790
Malonic acid	6

The above-formed color pixels gave a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

Further, after the same color-filter radiation-sensitive composition as the above color-filter radiation-sensitive composition was allowed to stand at room temperature for 3 days in the same manner as in Example 15, it gave a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

EXAMPLE 20

Green pixels were formed in the same manner as in Example 15 except that the color-filter radiation-sensitive composition was replaced with a color-filter radiation-sensitive composition shown in Table 18.

TABLE 18

Compound	part
Pigment C.I. Pigment Green 7	90
Binder Methacrylate/methacrylic acid/poly-styrene macromonomer (compositional weight ratio 65/25/10, average molecular weight Mw 40,000)	50
Radiation-sensitive compound Trimethylolpropane triacrylate (Biscoat 295, supplied by Osaka Organic Chemical Industry Ltd)	40
Solvent Organic carboxylic acid 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (I-369 supplied by Japan Ciba Geigy)	24
Organic carboxylic acid Diethylene glycol dimethyl ether	790
Citraconic acid	3
Mesaconic acid	3

The above-formed color pixels gave a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

Further, after the same color-filter radiation-sensitive composition as the above color-filter radiation-sensitive composition was allowed to stand at room temperature for 3 days in the same manner as in Example 15, it gave a color filter in which no undissolved substance remained in a non-pixel portion on the substrate.

What is claimed is:

1. A pigment-dispersed color-filter composition comprising an admixture of:

- (A) an alkali-soluble block copolymer composed of a block having an acid group and a block having no acid group;
- (B) a radiation-sensitive compound,
- (C) a pigment,
- (D) an organic medium, and
- (E) an aliphatic or aromatic dicarboxylic acid having a molecular weight of 1,000 or less.

2. The composition of claim 1, wherein the radiation-sensitive compound (B) is selected from the group consisting of a polymerization initiator which generates radicals under irradiation with radiation and is selected from a carbonium compound, an azo compound, an azide compound, an organic sulfur compound, a peroxide compound and a trihalomethane compound, and a photo-crosslinking agent having at least two functional groups which generate carbene or nitrene under irradiation with radiation.

3. The composition of claim 1, wherein the organic medium (D) is selected from the group consisting of ethyl lactate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, ethyl 2-ethoxypropionate, methylcellosolve acetate, ethylcellosolve acetate, diethylene

glycol dimethyl ether, diethylene glycol diethyl ether and propylene glycol monomethyl ether acetate.

4. The composition of claim 1, wherein the organic medium is present in an amount of at least 50% by wt. of the composition.

5. The composition of claim 1, wherein the aliphatic or aromatic dicarboxylic acid is selected from the group

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consisting of malonic acid, citraconic acid, itaconic acid, mesaconic acid, fumaric acid and phthalic acid.

6. The composition of claim 1, wherein the alkali-soluble block copolymer is a copolymer derived from benzyl methacrylate, methacrylic acid and polystyrene macromonomer, or a copolymer derived from methyl methacrylate, methacrylic acid and polystyrene macromonomer.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,368,976

DATED : November 29, 1994

INVENTOR(S) : Yusuke TAJIMA, et al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

On the title page, Item [75], the third inventor's name is spelled incorrectly. It should read:

--Fumitaka Takinishi--

Signed and Sealed this
Fourth Day of April, 1995

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 740 183 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
30.10.1996 Bulletin 1996/44

(51) Int. Cl.⁶: G02F 1/1335

(21) Application number: 96106302.1

(22) Date of filing: 22.04.1996

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL

(30) Priority: 24.04.1995 JP 120380/95
04.07.1995 JP 189743/95
25.08.1995 JP 239040/95

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(54) Composition for black matrix, formation of black matrix and article provided with black matrix

(57) A composition for a black matrix is disclosed. The composition is composed of a black pigment and a binder for the pigment. The black pigment is a compound-oxide black pigment, which comprises at least two metal oxides and has a spinel or inverse-spinel crystalline structure. Also disclosed are a process for the formation of a black matrix from the composition and an article provided with a black matrix so formed.

• Description

BACKGROUND OF THE INVENTION

5 a) Field of the Invention

This invention relates to a black-pigment-containing composition for the formation of a light-shielding black matrix on a liquid crystal (LC) display useful in a home or office image-receiving equipment such as a television or visual telephone, a video camera, a personal computer, an office equipment such as a word processor, or a display of a factory automation equipment, an automated store control equipment or a measuring equipment, a color filter of an image pick-up device or a display panel of a luminescent, full color or monochrome flat-panel display; a process for the formation of a black matrix; and an article provided with the black matrix.

More specifically, the present invention is concerned with a composition containing a black pigment and suitable for use in forming a black matrix on a filter substrate or a display panel of an LC display, a plasma address LC, a plasma display, a fluorescent display, a LED display, a CRT color display or an LC projector, said composition using as the black pigment a compound-oxide black pigment having excellent properties such as coloring power and light shielding property and superb fastness such as ultraviolet ray resistance, electron beam resistance, light resistance and heat resistance; a process for the formation of a black matrix by using the composition; and an article provided with the black matrix.

20 b) Description of the Related Art

In an LC color display or the like, it has heretofore been the practice to form, on a glass substrate for a color filter, a pixel pattern of three primary colors of a red color (hereinafter called "R"), a green color (hereinafter called "G") and a blue color (hereinafter called "B") in the form of a mosaic, stripe or the like for the dispersion of light, which has been transmitted from a fluorescent lamp as a back-light (light source), into spectra, so that white light from the fluorescent lamp is transmitted through the color filter and distributed into R, G and B lights and a image is displayed in full color by these distributed R, G and B lights.

In the case of a full color display panel for a luminescent flat panel display, a pixel pattern composed of R, G and B light-emitting elements is also formed on a rear glass substrate of the display panel. By lights emitted by phosphors of the three primary colors of R, G and B excited by ultraviolet rays, lights emitted by light-emitting diodes of the three primary colors of R, G and B or lights emitted by discharge gazes, an image is displayed in full color.

The method making use of a color filter having pixels of the three primary colors as described above, however, cannot avoid mutual overlapping of color lights from adjacent pixels in the color filter and hence mixing of R, G and B color lights, resulting in a deterioration in the separation of color lights by the pixels. Therefore, use of a color filter composed of R, G and B pixels alone inevitably results in a display panel which can produce only images inferior in definition and vividness.

In the case of an LC color display or the like, it has been attempted to overcome the above problem by surrounding R, G and B pixels, which are formed on a glass substrate of a color filter, with a black matrix.

Proposed as methods for the formation of a black matrix include (1) deposition of a metal such as chromium, (2) dyeing with a black dye, (3) printing with a printing ink containing carbon black, a dye mixed to present a black color, or the like, (4) photolithography making use of a photosensitive black resin composition.

The method (1) is accompanied with the drawbacks that it requires high cost, involves complex steps and cannot achieve an improvement in productivity, and requires large facilities and the like and hence high initial investment. The method (2) requires mixing of two or three dyes to attain dyeing in a black color because there is no good dye usable upon dyeing in a black color. Accordingly, this method cannot provide a black matrix having a black color of sufficient density or, even if such a black matrix is provided, its color is uneven. If a substrate on which a black matrix is formed is subjected to high-temperature treatment, the black matrix involves problems in physical properties such as heat resistance and light fastness. The method (2) therefore has not found commercial utility. As to the printing making use of a black pigment as the method (3) and the lithography making use of a photosensitive resin as the method (4), use of carbon black as the black pigment involves problems such as reduced light shielding property due to insufficient dispersion of carbon black in a black-matrix-forming composition, electrical conductivity inherent to carbon black and, where the content of carbon black is high, insufficient photocuring of a black-matrix-forming composition.

Further, black iron oxide as a black pigment is a material which is also called "magnenite". As this material has magnetic properties, particles of black iron oxide tend to coagulate in a dispersion medium due to their magnetic properties. Upon preparation of a composition for the formation of a black matrix, the pigment is hardly dispersible and, even when dispersed, the pigment has tendency to undergo premature coagulation. The black-matrix-forming composition so obtained therefore is accompanied with drawbacks such that it has inferior long-term dispersion stability, its coloring

power is low, its pigment has inferior stability to oxidation by air, and a black matrix formed from the composition are gradually lowered in blackness and their color changes to a brownish color.

Considering specifically a black matrix to be formed on a color filter for a luminescent flat panel display, the formation of the black matrix includes a high-temperature baking step so that conventional black dyes, mixed dyes of black color, organic black pigments, carbon black and the like cannot be used for the formation of the black matrix. Further, black iron oxide as a black pigment, when calcined at high temperatures, changes into red iron oxide which is an iron oxide of a brown or light brown color. On the other hand, titanium black which is another black pigment also changes into white titanium oxide at 300-350°C. Neither black dyes and pigments are hence usable as black matrix pigments which are required to have heat resistance sufficient to withstand a high-temperature calcination step.

The dyes and pigments which have heretofore been used as described above are therefore insufficient in performance as dyes for the formation of a black matrix are required to have excellent light shielding property, dispersibility, light fastness and the like.

SUMMARY OF THE INVENTION

With a view to overcoming the above-described various problems which have heretofore arisen upon formation of a black matrix, the present invention has as a primary object the provision of a black matrix which has excellent light shielding property and provides a displayed image with good definition and vividness.

To prevent mixing of the three primary colors at a display panel of an LC display or a luminescent flat panel display, the present inventors have proceeded with a variety of investigations on black pigments employed for the formation of a black matrix which surrounds pixels of the three primary colors. As a result, the present inventors have found that certain specific inorganic pigments are excellent in various physical and other properties for use in black matrices and are effective for the resolution of the above-described problems of the related art.

The present invention therefore provides a composition for a black matrix, said composition being composed of a black pigment and a binder for said pigment, wherein said black pigment is a compound-oxide black pigment comprising at least two metal oxides and having a spinel or inverse-spinel crystalline structure; a process for the formation of a black matrix, which makes use of the composition; and also an article provided with the black matrix.

According to the present invention, the composition which contains as a light shielding pigment the compound-oxide black pigment having excellent fastness and shielding property is excellent in optical properties such as blackness and optical density and is also superb in the dispersion stability in a dispersion medium. The use of the black-matrix-forming composition according to the present invention for the formation of a black matrix on a color filter of an LC display, a display panel of a luminescent flat panel display, or the like provides a black matrix - which is excellent in blackness and light shielding property and superb in fastness such as heat resistance, ultraviolet ray resistance, light resistance, chemical resistance and solvent resistance - more easily and economically compared with conventional processes. In particular, a black matrix on a display panel of a luminescent flat panel display or the like is formed by using an inorganic binder and conducting high-temperature baking. The above-described black pigment useful in the practice of the present invention is the best as a black pigment with heat resistance sufficient to withstand such high temperatures.

LC displays, luminescent flat panel display panels and the like fabricated using the black-matrix-forming composition, which pertains to the present invention and contains the compound-oxide black pigment, can achieve excellent color separation by their pixels and can hence produce images having excellent vividness and visibility.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The present invention will hereinafter be described more specifically based on certain preferred embodiments.

In the present invention, image display systems such as LD displays, plasma address LCs and LC projectors are called "LC displays", whereas image display systems such as plasma displays, fluorescent displays, LED displays and CRT color display panels are called "luminescent flat panel displays".

Further, color filter substrates or display panel substrates employed in these displays are called simply "substrates".

In the case of an LC color display, illustrative methods for the formation of a black matrix include a method in which a black matrix is formed in combination with an R, G and B pixel pattern of a color filter on a substrate and a method in which to increase the percent aperture of a pixel pattern, a black matrix is formed separately from the pixel pattern, for example, on a side of a TFT array substrate.

For a display panel of a luminescent flat panel display, there is a method in which a black matrix is applied to a rear glass substrate in registration with pixels of R, G and B light-emitting elements on a front glass substrate.

The black matrix composition according to the present invention is obtained by mixing or dispersing a the compound-oxide black pigment in a photosensitive or non-photosensitive resin varnish as will be described subsequently herein. Using this composition, a pattern is formed on a glass substrate for a color filter of an LC display, a display panel

of a luminescent flat panel display, or the like by a conventionally known method, whereby a desired black matrix can be formed.

A description will next be made of the compound-oxide black pigment employed in the black matrix composition according to the present invention.

The compound-oxide black pigment useful in the practice of the present invention is a pigment composed of two or more metal oxides and has been formed by conducting calcination at a high temperature. The compound-oxide black pigment has merits such that as a pigment, it is excellent in various properties such as chemical resistance, heat resistance, light resistance, water resistance and solvent resistance, possesses excellent properties such as coloring power, hiding power and light-shielding property, shows good dispersibility in a photosensitive varnish (organic binder) as a dispersion medium for the pigment, is also excellent in the storage stability of the resulting dispersion, and even when the dispersion is mixed in a photosensitive resin, it does not practically impair the photocurability of the varnish as the dispersion medium. Concerning heat resistance, in particular, the compound-oxide black pigment is superior to other black pigments and is stably usable up to about 800°C.

Upon fabrication of a color filter or the like, high-temperature heat treatment may be required, for example, when ITO electrodes are formed by deposition on a filter substrate or when a polyamic acid, a polyimide precursor, is used as a resin of a varnish or an oriented film for an LCD and imidation is conducted as post-treatment. The compound-oxide black pigment employed in the present invention is excellent in heat resistance so that it can be very stably used even at such high temperatures.

Such a black pigment remains stable in a high-temperature baking step upon formation of a black matrix on a display panel for a luminescent flat panel display and is therefore a pigment most suitable as a pigment for the formation of a black matrix.

Typical examples of the compound-oxide black pigment employed in the present invention include compound metal-oxide pigments of at least two metals selected as principal metal components from the group consisting of copper, chromium, iron, manganese, cobalt, aluminum, nickel, zinc, antimony, titanium, barium and the like. Each of these pigments has a spinel or inverse-spinel crystalline structure.

Specific examples of the compound-oxide black pigment include compound-oxide black pigments composed of copper and chromium as principal metal components, compound-oxide black pigments composed of copper and manganese as principal metal components, compound-oxide black pigments composed of copper, iron and manganese as principal metal components, compound-oxide black pigments composed of cobalt, chromium and iron as principal metal components, compound-oxide black pigments composed of cobalt, chromium, iron and manganese as principal metal components and compound-oxide black pigments composed of cobalt, nickel, chromium and iron. These pigments can be used either singly or in combination.

As pigments for the formation of a black matrix in the present invention, they are not limited to black pigments but even chromatic compound-oxides pigments can be used either singly or as mixtures obtained to have light shielding property provided that they are compound-oxide pigments capable of fully shielding visible lights emitted from R, G and B pixels, respectively. Upon mixing chromatic pigments to have light shielding property, these chromatic pigments alone can be mixed. It is also preferred to use one or more of the above-described black pigments as a mixture with chromatic pigments. As a hue obtained by mixing chromatic pigments to have light shielding property, a black color, a dark gray color or a dark chromatic color is desired to ensure absorption of visible light.

Illustrative examples of the above-described chromatic compound-oxide pigments include compound-oxide pigments such as C.I. Pigment Blue 28 (cobalt-aluminum system), C.I. Pigment Blue 36 (cobalt-aluminum-chromium system), C.I. Pigment Green 26 (cobalt-aluminum-chromium system), C.I. Pigment Green 50 (titanium-nickel-cobalt-zinc system), C.I. Pigment Brown 33 (iron-zinc-chromium system), and C.I. Pigment Brown 34 (iron-nickel-aluminum system). These pigments are also embraced by the expression "compound-oxide black pigment" in the present invention.

Each compound-oxide black pigment usable in the present invention can be obtained by any one of preparation processes consisting of a dry synthesis process, a wet synthesis process and a wet oxidation process. A description will hereinafter be made about these preparation processes and properties of pigments available from such processes.

According to the dry synthesis process, metal oxides as metal components for a pigment are mixed at a ratio as needed, followed by sintering at a high temperature. From example, the oxides, hydroxides, carbonates or the like of the metal components for the pigment are mixed at a desired ratio into an intimate mixture, the mixture is calcined at a temperature of about 600°C or higher, and sintered coarse particles so formed are ground into the pigment in a pulverizer. Primary particles of the pigment obtained by this process have an average particle size of from about 0.3 to 0.7 µm, and the BET specific surface area of the pigment is about 5 m²/g or so.

According to the wet synthesis process, on the other hand, salts of the metal components for the pigment are dissolved in the same aqueous medium, an alkaline agent is added to the solution to have the respective metal salts concurrently deposited as compounds convertible to oxides by heat treatment, such as their oxides, hydroxides or the like, and the mixture so deposited is calcined and then ground into the pigment. Primary particles of the pigment obtained by this preparation process have an average particle size of from about 0.1 to 0.4 µm, and the BET specific surface area of the pigment is about 25 m²/g or smaller.

Further, the wet oxidation process is a new synthesis process. According to this synthesis process, salts of at least two metals selected from copper, chromium, iron, manganese, cobalt, aluminum, nickel, zinc, antimony, titanium, barium or the like are dissolved in the same aqueous medium, an alkaline agent is added to the solution to have the mixed metal salts deposited as mixed hydroxides or the like. Either concurrently with the deposition or subsequent to the deposition, the metal hydroxides deposited in the liquid phase are subjected to oxidation treatment in the liquid phase, followed by calcination treatment, for example, calcination treatment at about 400°C to 650°C so that a pigment is obtained. Primary particles of the pigment obtained by this synthesis process have a BET specific surface area of at least 40 m²/g and an average particle size of from about 0.01 to 0.1 µm.

Depending on the type of a synthesis process such as that described above, the mean particle size and BET specific surface area of the resulting pigment vary. A pigment having a greater particle size like a pigment obtained by the dry process or the wet process makes it possible to provide a higher pigment content when the pigment is formulated into a pigment dispersion by dispersing it in a varnish as an organic binder. At substantially the same pigment content, the above pigment can lower the viscosity of the pigment dispersion. Since a conventional compound-oxide black pigment is generally an inorganic pigment, its coloring power is inferior to an organic pigment and due to its high specific gravity, its dispersion tends to develop its settling in the course of storage over a long period of time. The inorganic pigment obtained by the above-described wet oxidation process however has been formed into extremely fine particles, so that the extremely fine particles have been significantly improved in coloring power, blackness, dispersion stability and anti-settling stability and are most suited for the object of the present invention.

A description will now be made of a preferred embodiment of the preparation of a compound-oxide black oxide by the above-described wet oxidation process. First, as salts of individual metals for the compound-oxide black oxide, those employed upon preparation of compound-oxide pigments, such as sulfates, nitrates, carbonates, chlorides, acetates and the like can all be used. Salts of these individual metal components are dissolved in water to prepare a solution of the mixed salts. The total concentration of the salts of the metal components in the aqueous solution may suitably range from about 5 to 50 wt.% or so. As an alkaline agent used for the deposition of metal hydroxides from the aqueous solution of the above-described mixed salts, a caustic alkali such as caustic soda is preferred.

The mixed metal hydroxides are caused to deposit by the alkaline agent and are then subjected to oxidation treatment. Upon oxidation treatment, the efficiency of oxidation becomes higher as the concentration of the metal hydroxides becomes lower. A lower concentration of the metal hydroxides is therefore effective of the formation of the pigment as finer particles. For these reasons, the concentration of metal hydroxides upon oxidation treatment is suitably from 0.05 to 0.5 mole/liter as calculated based on the principal metal salts. The pH of the solution at the time of the deposition of the hydroxides or the oxidation treatment is preferably in a range of from 7 to 13. The preferred synthesis temperature of the metal hydroxides can be in a range of from 20 to 40°C and the heating preferred agent temperature thereof can be in a range of from 70 to 100°C.

In the wet oxidation process, it is essential to treat the mixed metal hydroxide, which has been caused to deposit by the alkaline agent, in such a way that their metal ions are each oxidized from a lower valence to a higher valence, for example, to convert divalent metal ions to trivalent metal ions. As an oxidizing agent for use in the above oxidation, any oxidizing agent can be used such as hydrogen peroxide, sodium peroxide, sodium chlorate, air or oxygen gas. However, an oxidizing agent which does not form any impurity by oxidation, for example, a hydrogen peroxide solution, air or oxygen gas is a preferred oxidizing agent.

Subsequent to the above-described oxidation treatment, the resultant oxide is filtered and dried. The filter cake so dried is then calcined. The calcination is conducted at 400-650°C for 30 minutes to 1 hour in an oxidizing atmosphere so that the dried dry cake is converted into a compound-oxide pigment having the perfect spinel structure. According to this wet oxidation process, the oxidizing treatment of the precipitated mixed metal hydroxides in the water phase makes it possible to form primary particles of the pigment of the single spinel structure as very fine particles even at a relatively low calcination temperature. The pigment so obtained is in the form of soft particles, thereby bringing about the merit that its dry grinding or wet milling is easy.

In the present invention, the compound-oxide black pigment can be surface-treated, as needed, with at least one coating material selected from the group consisting of at least one coating material selected from the group consisting of silicon oxide or vitreous inorganic materials, hardenable polymers, and polymers substantially insoluble in a medium.

The surface treatment of the compound-oxide black pigment with such a coating material makes it possible to impart properties such as chargeability and medium compatibility to the pigment. This improves the dispersibility of the pigment in a varnish as a dispersion medium upon preparation of the composition of this invention for the black matrix and also during storage of the composition, and also improves the re-dispersibility, dispersion stability and the like of the pigment subsequent to the storage of the composition. When the pigment is treated with a silicon oxide or vitreous inorganic material, the pigment exhibits improved compatibility with a low m.p. glass binder during calcination upon formation of a black matrix. This improved compatibility facilitates baking of the black matrix to a glass substrate.

Illustrative examples of the silicon oxide or vitreous inorganic material as a surface-treatment agent for the pigment include hydrogenated amorphous silica, anhydrous amorphous silica, mixtures thereof, and low m.p. vitreous materials.

The surface treatment of the pigment by the inorganic material can be carried out in a manner similar to a coating method for a conventionally-known pigment with silica or a vitreous material. For example, the compound-oxide black pigment is dispersed in a finely-divided form in water, and an aqueous solution of sodium silicate, potassium silicate or the like (with optional addition of an aqueous solution of lead nitrate) and a dilute aqueous solution of sulfuric acid are simultaneously dropped or poured into the dispersion, followed by stirring. As an alternative, the pigment is dispersed in a finely-divided form in a solvent such as ethanol, and tetraethyl orthosilicate, tetramethyl orthosilicate or the like (with optional addition of an organolead compound) is added to the dispersion so that the silicate is hydrolyzed and condensed to deposit as films on surfaces of the pigment. In this manner, the pigment is obtained in a coated form.

The black pigment has been almost uniformly surface-treated with amorphous silica, a low m.p. vitreous material or a mixture thereof as described above. Subsequent to the surface treatment, the black pigment is thoroughly washed with water to eliminate soluble salts and other water-soluble substances and after drying, is used for the formation of a black matrix.

The inorganic coating material is required in an amount sufficient to coat the surfaces of the black pigment. Specifically, the inorganic coating material is used in a proportion of 1-100 parts by weight, preferably 3-50 parts by weight per 100 parts by weight of the pigment. It is desired to treat the pigment with the coating material in an amount suitably chosen depending on the particle size and specific surface area of the particles of the pigment to be coated. The amount of the coating material to be used may be determined using as an index an oil absorption of the pigment to be coated. This coating can be conducted a plurality of times for the same black pigment.

Use of the coating material in an unduly small amount cannot sufficiently improve the dispersibility, dispersion stability and the like of the pigment. An unduly large amount, however, results in a lower content of the pigment in a resulting black-matrix-forming composition, and is not desired because the surface-treated pigment is required in a large amount to surely achieve a degree of pigmentation which is needed for a black matrix to be formed.

Hardenable polymers usable as coating materials include conventionally-known hardenable resins, for example, curable amino resins, curable epoxy resins, curable phenol resins, curable urethane resins, crosslinkable unsaturated polyester resins, and crosslinkable poly(meth)acrylate resins.

In addition, even non-hardenable polymers are usable as coating materials for the pigment, provided that they are substantially insoluble in solvents, chemicals or the like which are used in the fabrication steps of color filters. Illustrative examples of polymers substantially insoluble in these solvents include polyamide resins, polyimide resins, and polyamideimide resins.

Where these organic materials which can form such insoluble coating are hardenable resins, they are each used in a soluble form, for example, in the form of monomer(s), an initial condensation product or the like as known in the art, optionally in combination with an appropriate crosslinking agent, curing agent, catalyst, polymerization initiator or the like. In the case of non-hardenable polymers, each of them can be used in a form dissolved in a solvent in which the polymer is soluble.

The surface treatment of the compound-oxide black pigment by such an organic coating material is conducted by dispersing the pigment in a finely-divided form in water or a solvent, dropping or pouring the organic coating material into the dispersion under stirring in a manner commonly employed for the formation of coating, for example, in the form of an aqueous solution, an emulsion, a solvent solution or the like, optionally heating the resultant mixture, and then adding a curing agent such as an amine, curing catalyst such as an alkali or a polymerization initiator.

The coated pigment so obtained has been almost uniformly surface-treated with the polymer which is substantially insoluble in the medium. Similarly to the foregoing, this polymer is also required in an amount sufficient to coat the surfaces of the black pigment. Specifically, the polymer is used in an amount of 1-100 parts by weight, preferably 3-50 parts by weight per 100 parts by weight of the pigment. The amount of the polymer to be used may be determined using as an index the particle size, specific surface area and oil absorption of the pigment to be coated.

This coating with the silicon oxide or vitreous inorganic material, hardenable polymer or insoluble polymer can be conducted a plurality of times for the same black pigment.

Subsequent to the surface treatment, the coated pigment is thoroughly washed with water to eliminate soluble salts and other water-soluble substances and after drying, is used for the formation of a black matrix.

As has been described above, it is one of the merits of the compound-oxide black pigment that as a result of the calcination of the pigment at a high temperature, the pigment is composed of a compound metal oxide having the specific crystalline structure. It therefore has high heat resistance as a pigment and exhibits sufficient heat resistance even at temperatures where organic substances burn off upon formation of a black matrix, for example, at 450-900°C.

Therefore, when a display panel is fabricated by subjecting a black matrix to high-temperature treatment subsequent to its patterning as in the case of a display panel for a luminescent flat panel display, a composition according to the present invention in which the compound-oxide black pigment is added with a low m.p. glass frit as an inorganic binder, an organosilica compound such as ethoxy silica and an organolead compound can be effectively used for the formation of the black matrix. It is also possible to form a black matrix by coating beforehand a substrate with a low m.p. glass frit over the entire surface thereof or on regions where the matrix is to be formed, patterning the black matrix with the composition according to the present invention and then baking the thus-patterned composition.

The low m.p. glass frit employed as a binder for the pigment in the composition according to the present invention can be, for example, fine powder of a lead borosilicate glass formed of lead oxide, silicon oxide and boron silicate as principal components. Depending on the composition, such glass frits range from a low-temperature baking glass frit whose baking temperature is about 500°C to a high-temperature baking glass frit whose baking temperature is about 700°C. These frits have been added with sodium oxide, titanium oxide, zirconium oxide, lithium oxide, aluminum oxide and/or the like as subordinate components.

Regarding the black-matrix-forming composition according to the present invention, its formulation, varnish and additives are determined depending on the coating method of the composition on a substrate, the formation method of the pattern.

Illustrative examples of the method for printing the black matrix composition according to the present invention on a substrate for the formation of a black matrix include various printing methods such as stencil screen printing, intaglio gravure printing, offset intaglio printing, offset lithographic printing and letterpress printing; electrodeposition; electronic printing; electrostatic printing; and thermal transfer.

The black-matrix-forming composition according to the present invention can be converted into a photosensitive black-matrix-forming composition by using a photosensitive resin as at least a portion of its binder. For the formation of a black matrix from the photosensitive black-matrix-forming composition of the present invention by photolithography, the composition is coated over the entire surface of a substrate by spin coating, roll coating or the like and, subsequent to formation of a rough pattern by photolithography, a printing method, thermal transfer or the like, a precise pattern is then formed by photolithography.

Usable components for the composition according to the present invention include, in addition to the compound-oxide black pigment and the inorganic binder, a varnish as an organic binder for dispersing the pigment. As the varnish, a suitable, conventionally-known, non-photosensitive or photosensitive varnish is chosen depending on the coating method and the pattern forming method.

Illustrative examples of the non-photosensitive varnish include varnishes useful in printing inks such as stencil screen inks, intaglio gravure inks, offset lithographic inks and letterpress inks; varnishes useful for electrodeposition; varnishes useful in developers for electronic printing and electrostatic printing; and varnishes useful in thermal transfer ribbons. Illustrative examples of the photosensitive varnish include photosensitive resin varnishes useful in ultraviolet ray curing inks, electron beam curing inks and the like. Besides these varnishes, varnishes suited for the above-described coating methods and photolithographic methods can also be used.

Illustrative examples of the non-photosensitive binder include cellulose acetate butyrate resins, nitrocellulose resins, styrene (co)polymers, polyvinyl butyral resins, aminoalkyd resins, polyester resins, amino-resin-modified polyester resins, polyurethane resins, acrylic polyol urethane resins, soluble polyamide resins, soluble polyimide resins, casein, hydroxyethylcellulose, water-soluble salts of styrene-maleate ester copolymers, water-soluble salts of (meth)acrylate ester (co)polymers, water-soluble aminoalkyd resins, water-soluble amino-resin-modified polyester resins, and water-soluble polyamide resins. These binders can be used either singly or in combination. The black-matrix-forming composition according to the present invention can be obtained by mixing, dispersing and kneading the compound-oxide black pigment with the binder by a conventionally-known method.

Illustrative examples of a photosensitive resin varnish usable in the black-matrix-forming composition according to the present invention include ultraviolet ray curing inks, electron beam curing inks and the like. Particularly preferred are photosensitive resin varnishes which are used for the formation of patterns by photolithography and etching. Specific examples include varnishes obtained by adding conventionally-known multifunctional acrylic monomers as reactive diluents to photosensitive cyclizing rubber resins, photosensitive phenol resins, photosensitive (meth)acrylic resins, photosensitive styrene-(meth)acrylic resins, photosensitive polyamide resins, photosensitive polyimide resins, photosensitive unsaturated polyester resins, polyester acrylate resins, polyepoxy acrylate resins, polyurethane acrylate resins, polyether acrylate resins and polyol acrylate resins; and varnishes obtained by adding an organic solvent or an aqueous medium to the first-mentioned varnishes as needed. The photosensitive black-matrix-forming composition according to the present invention can be obtained by adding a photopolymerization initiator such as benzoin ethyl ether or benzophenone to a mixture of the compound-oxide black pigment and the varnish and then kneading the resultant mixture by a conventionally-known method.

To form a black matrix by using the above-described photosensitive black-matrix-forming composition, the composition is evenly coated on a substrate by a coating method such as spin coating or roll coating and subsequent to pre-drying, a photomask is applied in close contact with the thus-coated substrate, followed by exposure and curing under an extra-high pressure mercury lamp. The resulting layer is then subjected to development and washing and, if necessary, further to post baking, whereby a black matrix can be formed.

Use of a thermal polymerization initiator in place of the photopolymerization initiator makes it possible to provide a thermally-polymerizable, black-matrix-forming composition according to the present invention.

The proportion of the organic binder in the black-matrix-forming composition according to the present invention is in a range of from 5 to 300 parts by weight, preferably from 10 to about 200 parts by weight per 100 parts of the compound-oxide black pigment.

In the case of the black-matrix-forming composition according to the present invention in which the low m.p. glass frit as an inorganic binder is used as a binder, the proportion of the inorganic binder is in a range of from 5 to 200 parts by weight, preferably from 10 to about 100 parts by weight per 100 parts by weight of the pigment. As a calcination temperature upon forming a black matrix with the composition, it is desired to calcine at a temperature such that the organic binder contained in the composition is burnt off in its entirety, the inorganic binder also contained in the composition is molten and the compound-oxide black pigment is fixed on a substrate. For example, about 450-900°C is desired as the calcination temperature.

Black matrices formed as described above are suited especially for various color displays. They are useful as color filters for LC displays and also as black matrices for LC displays, LC projectors, plasma address LCs and the like. They can also be used as color plasma display panels, that is, display panels in luminescent flat panel displays and also as black matrices in fluorescent display color display panels, luminescent diode color display panels, CRT color display panels and the like, whereby they can eliminate color blurring or color overlapping in displayed images and can provide the displayed images with vividness and good definition.

The article, which pertains to the present invention and is provided with the black matrix, is characterized in that a black matrix has been formed on a color filter of an LC display or a display panel of a luminescent flat panel display, such as that described above, by using the above-described black-matrix-forming composition according to the present invention.

A fabrication process of an LC color display will now be described based on one example thereof. An R, G and B color filter and a black matrix are formed on a color filter substrate. An oriented film for the LC color display is formed, followed by rubbing treatment, the printing of seals and the formation of transfer electrodes. On an array substrate, on the other hand, TFT elements are formed, followed by the formation of an oriented film for the LC color display, rubbing treatment, and the spreading of a spacer. The array substrate and the color filter substrate are then bonded together, followed by the filling of a liquid crystal, the sealing of cells, the bonding of polarizers, etc. so that a color LC panel is obtained. Through a module assembly step in which an integrated driver circuit and an integrated control circuit are connected to the panel and an illuminating backlight or the like is mounted, an LC color display is fabricated.

R, G and B coloring compositions for the formation of R, G and B pixels on a color filter can be those known to date, and the formation of the individual pixels can be conducted by a conventionally known method. Preferred examples of usable R, G and B pigments include C.I. Pigment Red 122, 123, 149, 177, 179, 190, 194, 207, 209 and so on; C.I. Pigment Yellow 24, 108, 109, 110, 166 and so on; C.I. Pigment Green 7, 36, 37 and so on; and C.I. Pigment Blue 15, 60, 66 and so on.

The pixels of the color filter are not limited to a combination of the three primary colors, and other combinations such as those of three primary colors of indigo-blue, magenta and yellow are of course feasible.

In the case of a color filter for an LC display or a like filter, the black-matrix-forming composition according to the present invention can be added further with one or more conventionally-known pigments, for example, to provide the resulting black matrix with an increased blackness so that a higher optical density can be obtained. Preferred as usable pigments are those having excellent fastness, superb electrical and physical properties, high coloring power, and a black color or a hue permitting easy toning into a black color. Illustrative examples of black pigments include C.I. Pigment Black 6, 7, 8, 9 and 10, the azomethineazo black pigments disclosed in Japanese Patent Publication (Kokoku) No. HEI 4-15265, and C.I. Pigment Black 31 and 32.

As an example of fabrication of a display panel for a luminescent flat panel display, a description will next be made of fabrication of a display panel for a color plasma display.

Using the black-matrix-forming composition according to the present invention, a black matrix of a grid pattern is formed on a front glass substrate by a method similar to that described above. Formed next are transparent electrodes, metal electrodes, a transparent dielectric layer, stripe partitions, seal layers, and a magnesium oxide layer. Formed on a rear glass substrate are data electrodes, a white dielectric layer, stripe partitions, blue, green and red phosphor layers, and seal layers. The thus-formed front glass substrate and rear glass substrate are assembled. Sealing, evacuation and gas filling steps are then performed. The assembly so obtained is connected to a circuit unit so that a display panel for a color plasma display is fabricated.

R, G and B compositions for the formation of R, G and B pixels on a display filter of a luminescent flat panel display can be those known to date, and the formation of the individual pixels can be conducted by a conventionally known method. For example, preferred examples of phosphor pigments usable for color plasma display panels include $(Y,Gd)BO_3:Eu$ as a red phosphor, $BaAl_{12}O_{19}:Mn$ and $Zn_2SiO_4:Mn$ as green phosphors, and $BaMgAl_{14}O_{23}:Eu^{2+}$ and $BaMg_2Al_{16}O_{27}:Eu$ as blue phosphors. Further, illustrative LEDs include InGaN-system blue LEDs, GaAlAs-system red LEDs, and GaP-system green LEDs.

The present invention will next be described more specifically by the following Synthesis Examples and Examples of pigments useful in the practice of the present invention. All designations of "part" or "parts" and "%", which will follow, refer to part or parts by weight and wt.% unless specified otherwise.

• Synthesis Example 1

A copper-iron-manganese compound-oxide black pigment (C.I. Pigment Black 26) was synthesized by a wet synthesis process. Specifically, measured were 120 parts of copper sulfate, 104 parts of iron sulfate heptahydrate and 170 parts of manganese sulfate. They were completely dissolved in about 800 parts of water, whereby an aqueous solution of the mixed salts was prepared. Next, 240 parts of caustic soda were measured as a precipitant and were then dissolved in about 800 parts of water, so that an aqueous solution was prepared. Further, 800 parts of water were provided, to which the aqueous solution of the mixed salts and aqueous solution of caustic soda, both prepared above, were simultaneously added dropwise under stirring at 26°C. A precipitation reaction was brought to completion in about 10 minutes to 1 hour.

The reaction mixture was filtered and the resulting filtrate was washed with water to thoroughly wash away soluble salts, whereby a filter cake was obtained. This filter cake was dried at 100-120°C for 8 hours or longer. The dried filter cake so obtained was calcined at 520°C for 1 hour in an oxidizing atmosphere. Primary particles of a copper-iron-manganese compound-oxide black pigment (hereinafter called "BK-1") so obtained had an average particle size of about 0.1 µm and a BET surface area of about 25 m²/g.

• Synthesis Example 2

In a manner as in Synthesis Example 1, a copper-chromium compound oxide (C.I. Pigment Black 28) was synthesized. Caustic soda was added as a precipitant to an aqueous solution of copper sulfate and chromium sulfate to conduct a precipitation reaction. Subsequent to filtration, water washing and drying, the dried filter cake so obtained was calcined at 520°C. Primary particles of a copper-chromium compound-oxide black pigment (hereinafter called "BK-2") so obtained had an average particle size of about 0.2 µm.

• Synthesis Example 3

In a manner as in Synthesis Example 1, a cobalt-chromium-iron compound oxide was synthesized. Caustic soda was added as a precipitant to an aqueous solution of cobalt sulfate, chromium sulfate and iron sulfate to conduct a precipitation reaction. Subsequent to filtration, water washing and drying, the dried filter cake so obtained was calcined at 520°C. Primary particles of a cobalt-chromium-iron compound-oxide black pigment (hereinafter called "BK-3") so obtained had an average particle size of about 0.05 µm.

• Synthesis Example 4

In a manner as in Synthesis Example 1, a cobalt-chromium-iron-manganese compound oxide was synthesized. Caustic soda was added as a precipitant to an aqueous solution of cobalt sulfate, chromium sulfate, iron sulfate and manganese sulfate to conduct a precipitation reaction. Subsequent to filtration, water washing and drying, the dried filter cake so obtained was calcined at 520°C. Primary particles of a cobalt-chromium-iron-manganese compound-oxide black pigment (hereinafter called "BK-4") so obtained had an average particle size of about 0.1 µm.

• Synthesis Example 5

In a manner as in Synthesis Example 1, a cobalt-nickel-chromium-iron compound oxide was synthesized. Caustic soda was added as a precipitant to an aqueous solution of cobalt sulfate, nickel sulfate, chromium sulfate and iron sulfate to conduct a precipitation reaction. Subsequent to filtration, water washing and drying, the dried filter cake so obtained was calcined at 520°C. Primary particles of a cobalt-nickel-chromium-iron compound-oxide black pigment (hereinafter called "BK-5") so obtained had an average particle size of about 0.1 µm.

• Synthesis Example 6

A copper-iron-manganese compound-oxide black pigment was synthesized in the form of fine particles by a wet synthesis process. Specifically, measured were 120 parts of copper sulfate, 104 parts of iron sulfate heptahydrate and 170 parts of manganese sulfate. They were completely dissolved in about 800 parts of water, whereby an aqueous solution of the mixed salts was prepared. Next, 240 parts of caustic soda were measured as a precipitant and were then dissolved in about 800 parts of water, so that an aqueous solution was prepared. Further, 800 parts of water were provided, to which the aqueous solution of the mixed salts and aqueous solution of caustic soda, both prepared above, were simultaneously added dropwise under stirring at 26°C. A precipitation reaction was conducted at pH 12 for about 30 minutes to 1 hour. After completion of the dropwise addition, 100 parts of a 35% aqueous solution of hydrogen per-

oxide were added dropwise while maintaining the pH, whereby oxidation treatment was conducted. Completion of the oxidation reaction at that time was confirmed by measuring an oxidation-reduction potential.

After the completion of the oxidation treatment, the temperature of the reaction mixture was changed to 70°C and aging was then conducted for about 1 hour or so. The reaction mixture was then filtered and the resulting filtrate was washed with water to thoroughly wash away soluble salts, whereby a filter cake was obtained. This filter cake was dried at 100-120°C for 8 hours or longer. The dried filter cake so obtained was calcined at 520°C for 1 hour in an oxidizing atmosphere. A pigment so obtained was in the form of small primary particles, whose particle sizes ranged from about 0.01 to 0.06 µm. Their BET specific surface area was about 56 m²/g. The pigment was a copper-iron-manganese compound-oxide, fine particulate black pigment (hereinafter called "BK-6") which had good blackness, coloring power and dispersibility and showed a bluish black color.

Synthesis Example 7

In a manner as in Synthesis Example 6, 120 parts of copper sulfate, 104 parts of iron sulfate heptahydrate and 170 parts of manganese sulfate were measured. They were completely dissolved in about 800 parts of water, whereby an aqueous solution of the mixed salts was prepared. Next, 240 parts of caustic soda were measured as a precipitant and were then dissolved in about 800 parts of water, so that an aqueous solution was prepared. Further, 800 parts of water were provided, to which the aqueous solution of the mixed salts and aqueous solution of caustic soda, both prepared above, were simultaneously added dropwise under stirring while maintaining the resulting mixture at 26°C. A precipitation reaction was conducted at pH 12. After completion of the precipitation reaction, the reaction mixture was bubbled under stirring while feeding air at a flow rate of 50 liters/min through a bottom of a reaction tank, so that oxidation treatment was conducted. Completion of the oxidation reaction at that time was confirmed by monitoring an oxidation-reduction potential.

After the completion of the oxidation treatment, the temperature of the reaction mixture was changed to 70°C and aging was then conducted for about 1 hour or so. The reaction mixture was then filtered and the resulting filtrate was washed with water to thoroughly wash away soluble salts, whereby a filter cake was obtained. This filter cake was dried at 100-120°C for 8 hours or longer. The dried filter cake so obtained was calcined at 520°C for 1 hour in an oxidizing atmosphere. A pigment so obtained was in the form of small primary particles, whose particle sizes ranged from about 0.01 to 0.05 µm. Their BET specific surface area was about 60 m²/g. The pigment was a copper-iron-manganese compound-oxide, fine particulate black pigment (hereinafter called "BK-7") which had good blackness, coloring power and dispersibility and showed a bluish black color.

Synthesis Example 8

In a manner as in Synthesis Example 6, 120 parts of copper sulfate and 227 parts of manganese sulfate were measured. They were completely dissolved in about 800 parts of water, whereby an aqueous solution of the mixed salts was prepared. Next, 240 parts of caustic soda were measured as a precipitant and were then dissolved in about 800 parts of water, so that an aqueous solution was prepared. Further, 800 parts of water were provided, to which the aqueous solution of the mixed salts and aqueous solution of caustic soda, both prepared above, were simultaneously added dropwise while maintaining the resulting mixture at 26°C. A precipitation reaction was conducted at pH 12. After completion of the dropwise addition, a 35% aqueous solution of hydrogen peroxide was added dropwise while maintaining the pH, whereby oxidation treatment was conducted.

After the completion of the oxidation treatment, the temperature of the reaction mixture was changed to 70°C and aging was then conducted for about 1 hour or so. The reaction mixture was then filtered and the resulting filtrate was washed with water to thoroughly wash away soluble salts, whereby a filter cake was obtained. This filter cake was dried at 100-120°C for 8 hours or longer and further, was calcined at 520°C for 1 hour in an oxidizing atmosphere. A pigment so obtained was in the form of small primary particles, whose particle sizes ranged from about 0.01 to 0.08 µm. Their BET specific surface area was about 42 m²/g. The pigment was a copper-manganese compound-oxide, fine particulate black pigment (hereinafter called "BK-8") which had good blackness, coloring power and dispersibility and showed a bluish black color.

Synthesis Example 9

The compound-oxide black pigment "BK-1" obtained in Synthesis Example 1 was surface-treated with a siliceous material. Specifically, five hundred parts of the black pigment "BK-1" were taken, to which 3 parts of an aqueous solution of sodium silicate (29% as silicic anhydride) and 1,000 parts of water were added to wet the pigment. The pigment was thoroughly dispersed in an attritor filled with steel balls until the mixture became a uniform flowable slurry. The slurry so obtained was caused to pass through a screen, whereby the slurry was separated from the steel balls. The slurry was diluted with water to give a total volume of 10,000 parts by volume. On the side, 380 parts of an aqueous

solution of sodium silicate (29% as silicic anhydride) were diluted with water to give a total volume of 1,700 parts by volume.

Further, 1,700 parts of a 3.30% aqueous solution of sulfuric acid were provided. The pigment dispersion was heated to 90°C, to which a dilute aqueous solution of sodium hydroxide was added to adjust the pH to 10.0. To the mixture so obtained, the dilute aqueous solution of sodium silicate and the dilute aqueous solution of sulfuric acid, both prepared above, were added dropwise. Their dropped amounts were controlled so that the reaction mixture remained alkaline. Subsequent to completion of the addition of both the solutions, stirring was continued for 1 hour, followed by the addition of dilute sulfuric acid to adjust the pH to 6.5-7.0. The slurry so obtained was filtered. The resulting filter cake was washed until soluble salts were eliminated, followed by drying, whereby 600 parts of a silica surface-treated, black, fine particulate compound-oxide pigment (hereinafter called "BK-9") were obtained. The amount of silica so coated was about 20% based on the pigment.

Synthesis Example 10

To 500 parts of the compound-oxide black pigment "BK-1" obtained in Synthesis Example 1, 1,000 parts of a 10% aqueous solution of methanol, said solution containing 10 parts of an anionic dispersant, were added, whereby the pigment was wetted. Further, 4,000 parts of water were added, followed by thorough dispersion of the resultant mixture in an attritor filled with steel balls until the mixture became a uniform viscous slurry. The slurry so obtained was caused to pass through a screen, whereby the slurry was separated from the steel balls. The slurry was diluted with water to give a total volume of 10,000 parts by volume. On the side, 167 parts of an aqueous solution of sodium silicate (30% as silicic anhydride) were diluted with water to give a total volume of 1,000 parts by volume. Further, 1,000 parts of a 2.50% aqueous solution of sulfuric acid were provided.

Similarly to the surface treatment method for the pigment in Synthesis Example 6, the pigment dispersion which had been heated to 90°C was adjusted to pH 10.0 with a dilute aqueous solution of sodium hydroxide. To the mixture so obtained, the dilute aqueous solution of sodium silicate and the dilute aqueous solution of sulfuric acid, both prepared above, were added dropwise under control so that the reaction mixture remained alkaline. Subsequent to completion of the addition of both the solutions, stirring was continued for 1 hour, followed by the addition of dilute sulfuric acid to adjust the pH to 6.5-7.0. The slurry so obtained was filtered. The resulting filter cake was washed, followed by drying, whereby 550 parts of a surface-treated, black compound-oxide pigment (hereinafter called "BK-10") were obtained. The amount of the surface treatment material was about 10% based on the pigment. When the frictional electricity of "BK-10" so obtained was measured by the blow-off method, a negative value was indicated so that an improvement in electrical insulating property was observed.

Synthesis Example 11

Similarly to the surface treatment method for the pigment in Synthesis Example 9, 500 parts of the fine particulate, compound-oxide black pigment "BK-6" obtained in Synthesis Example 6 were taken, to which a 10% aqueous solution of methanol, said solution containing an anionic dispersant, and water were added. The pigment was thoroughly dispersed in an attritor, followed by the dilution with water to give a total volume of 1,000 parts by volume. On the side, 167 parts of an aqueous solution of sodium silicate were diluted with water to give a total volume of 1,000 parts by volume. Further, 1,000 parts of a 2.50% aqueous solution of sulfuric acid were provided. Similarly to the surface treatment method for the pigment in Synthesis Example 9, the pigment dispersion which had been heated to 90°C was adjusted to pH 10.0 with a dilute aqueous solution of sodium hydroxide. To the mixture so obtained, the dilute aqueous solution of sodium silicate and the dilute aqueous solution of sulfuric acid, both prepared above, were added dropwise under control so that the reaction mixture remained alkaline. Subsequent to completion of the addition of both the solutions, the resulting mixture was stirred for 1 hour, followed by the adjustment to pH 6.5-7.0 with dilute sulfuric acid. The slurry so obtained was then filtered. The resulting filter cake was washed, followed by drying, whereby 550 parts of a surface-treated, black compound-oxide pigment (hereinafter called "BK-11") were obtained. The amount of the surface treatment material was about 10% based on the pigment. When the frictional electricity of "BK-11" so obtained was measured by the blow-off method, a negative value was indicated so that an improvement in electrical insulating property was observed.

Synthesis Example 12

The compound-oxide black pigment "BK-6" obtained in the form of fine particles in Synthesis Example 6 was surface-treated with a siliceous material. Specifically, like the surface treatment method for the pigment in Synthesis Example 6, an aqueous solution of sodium silicate and water were added to the black pigment "BK-6". The pigment was dispersed in an attritor, followed by the dilution with water. On the side, a dilute aqueous solution of sodium silicate and a dilute aqueous solution of sulfuric acid were provided. The pigment dispersion was heated to 90°C and its pH was

adjusted to 10.0 by addition of a dilute aqueous solution. To the mixture so obtained, the dilute aqueous solution of sodium silicate and the dilute aqueous solution of sulfuric acid, both obtained above, were added dropwise. Subsequent to completion of the addition of both the solutions, stirring was continued for 1 hour, followed by the adjustment of the pH to 6.5-7.0 with dilute sulfuric acid. The slurry so obtained was filtered, and the resulting filter cake was washed and then dried. A silica surface-treated, black, fine particulate compound-oxide pigment (hereinafter called "BK-12") were obtained. The amount of silica so coated was about 30% based on the pigment.

Synthesis Example 13

The compound-oxide black pigment "BK-7" obtained in the form of fine particles in Synthesis Example 7 was surface-treated with melamine resin layers. Specifically, fifty parts of an 70% aqueous solution of methylated methyolmelamine were diluted and dissolved in 50 parts of water. To the solution so obtained, 2.5 parts of glycine, 1.4 parts of a 7% aqueous solution of hydrochloric acid and 10 parts of water were added, followed by reaction at 50-55°C. After polycondensation was conducted until an initial condensation product crystallized out in chilled water, 7.6 parts of a 20% aqueous solution of sodium hydroxide and 3.5 parts of water were added for neutralization so that the reaction was suspended. The solution had a solid content of about 30% and, even when diluted with water, it remained in a clear solution form. Two hundred parts of the resin solution were added with water to give a total volume of 600 parts, whereby a resin solution of a methylolmelamine initial condensation product was obtained for the treatment of the pigment.

One hundred parts of the compound-oxide black pigment "BK-7" obtained in the form of fine particles in Synthesis Example 7 were taken, to which 200 parts of a 10% aqueous solution of methanol, said solution containing 10 parts of an anionic dispersant, were added, whereby the pigment was wetted. Further, 1,700 parts of water were added, followed by thorough deflocculation and dispersion. The resultant dispersion was then charged in a reaction vessel and its pH was adjusted to pH 4.5-5 with an aqueous solution of acetic acid. At 80-90°C, 600 parts of the above-described resin solution were added dropwise over 4 hours. Further, the pH was adjusted to 4.5-5 with an aqueous solution of acetic acid, followed by stirring for 3 hours to cure coatings. Filtration, water washing and drying were then conducted, whereby 130 parts of a surface-treated, compound-oxide black pigment (hereinafter called "BK-13") were obtained. The amount of the surface treatment material was about 30% based on the pigment. When the frictional electricity of "BK-13" so obtained was measured by the blow-off method, a positive value was indicated so that an improvement in electrical insulating property was observed.

Synthesis Example 14

The compound-oxide black pigment "BK-2" obtained in Synthesis Example 2 was surface-treated with melamine resin films. Specifically, following the treatment method for the pigment in Synthesis Example 13, 100 parts of the copper-chromium compound-oxide black pigment "BK-2" were added with 200 parts of a 10% aqueous solution of methanol, said solution containing 2 parts of an anionic dispersant, whereby the pigment was wetted. Further, 1,700 parts of water were added, followed by thorough deflocculation and dispersion. The resultant dispersion was then charged in a reaction vessel and its pH was adjusted to pH 4.5-5 with an aqueous solution of acetic acid. At 80-90°C, 300 parts of the pigment-treating resin solution of the methylolmalamine initial condensation product, said resin solution having been employed in Synthesis Example 12, were added dropwise over 2 hours. Further, the pH was adjusted to 4.5-5 with an aqueous solution of acetic acid, followed by stirring for 3 hours to cure coatings. Filtration, water washing and drying were then conducted, whereby 115 parts of a surface-treated, compound-oxide black pigment (hereinafter called "BK-14") were obtained. The amount of the surface treatment material was about 15% based on the pigment. When the frictional electricity of "BK-14" so obtained was measured by the blow-off method, a positive value was indicated so that an improvement in electrical insulating property was observed.

Synthesis Example 15

The compound-oxide black pigment "BK-1" obtained in Synthesis Example 1 was surface-treated with epoxy resin coatings. Specifically, using a reaction product between a liquid epoxy resin composed primarily of bisphenol A diglycidyl ether and sodium aspartate, 300 parts of its 10% aqueous solution were provided as an aqueous epoxy resin solution for the treatment of the pigment. As in Synthesis Example 13, 100 parts of the compound-oxide black pigment "BK-1" were added with a 10% aqueous solution of methanol, said solution containing an anionic dispersant, and also with water, followed by thorough deflocculation and dispersion.

The resultant dispersion was then charged in a reaction vessel. At room temperature, 300 parts of the epoxy resin solution were added dropwise over 1 hour. The resulting mixture was heated to 50°C, at which a 2% aqueous solution of hexamethylenediamine was added dropwise over 1 hour, followed by stirring at 60°C for 3 hours to cure coatings. Filtration, water washing and drying were then conducted, whereby 115 parts of a surface-treated, compound-oxide black pigment (hereinafter called "BK-15") were obtained. The amount of the surface treatment material was about 15%

based on the pigment. When the frictional electricity of "BK-1" so obtained was measured by the blow-off method, a positive value was indicated so that an improvement in electrical insulating property was observed.

Synthesis Example 16

In a manner as in Synthesis Example 1, blue, green and brown pigments, which were composed of compound oxides, respectively, were synthesized.

Specifically, C.I. Pigment Blue 28 composed of a cobalt-aluminum compound oxide was synthesized. Namely, caustic soda was added as a precipitant to an aqueous solution of cobalt sulfate and aluminum sulfate to conduct a precipitation reaction. After filtration, water washing and drying, the resulting filter cake was calcined at 520°C. Primary particles of the thus-obtained blue pigment (hereinafter called "BL-2") had an average particle size of about 0.1 µm.

C.I. Pigment Green 26 composed of a cobalt-aluminum-chromium compound oxide was synthesized. Namely, caustic soda was added as a precipitant to an aqueous solution of cobalt sulfate, aluminum sulfate and chromium sulfate to conduct a precipitation reaction. After filtration, water washing and drying, the resulting filter cake was calcined at 520°C. Primary particles of the thus-obtained green pigment (hereinafter called "GR-2") had an average particle size of about 0.2 µm.

C.I. Pigment Brown 33 composed of an iron-zinc-chromium compound oxide was synthesized. Namely, caustic soda was added as a precipitant to an aqueous solution of iron sulfate, zinc sulfate and chromium sulfate to conduct a precipitation reaction. After filtration, water washing and drying, the resulting filter cake was calcined at 520°C. Primary particles of the thus-obtained brown pigment (hereinafter called "BR-1") had an average particle size of about 0.2 µm.

Example 1

To fabricate an LC display having a color filter which was provided with a black matrix, pigments, that is, the compound-oxide black pigment "BK-1" obtained in Synthesis Example 1, a red pigment "R-1", a green pigment "G-1" and a blue pigment "BL-1" were separately dispersed in portions of a photosensitive resin varnish composed primary of a polyurethane acrylate resin by a three-roll mill, whereby four UV-curing, colored compositions were prepared. Proportioning was conducted in accordance with the following formula.

Component	Bk	R	G	B
Compound-oxide black pigment "BK-1"	25	-	-	-
Red pigment "R-1" (C.I. Pigment Red 149)	-	15	-	-
Green pigment "G-1" (C.I. Pigment Green 36)	-	-	20	-
Blue pigment "BL-1" (C.I. Pigment Blue 15)	-	-	-	10
Polyurethane acrylate resin varnish	30	30	30	30
Trimethylolpropane triacrylate	10	10	10	10
Neopentyl glycol diacrylate	5	5	5	5
Hydroxy-2-methylpropylphenone	2	2	2	2
2,2-Diethoxyacetophenone	1	1	1	1
Isopropyl alcohol	13	20	17	23
Toluene	7	10	8	12
Ethyl acetate	7	7	7	7
Total	100	100	100	100

To investigate performance as a black matrix for an LC display, the above black-matrix-forming composition was coated by a roll coater on a glass substrate, which had been subjected to surface treatment with a silane coupling agent, over the entire surface thereof to a wet thickness of 5 µm, followed by predrying at 60°C for 5 minutes. Full-surface exposure was conducted at a light quantity of 400 mJ/cm² under a 250 W extra-high pressure mercury lamp. The blackness of the resultant coating film was measured by a Macbeth densitometer. A value of 3.0 was indicated. The glass substrate with the coating film formed thereon was placed in front of a fluorescent lamp to investigate its light

shielding property. Light from the lamp was completely shielded, thereby demonstrating excellent performance as a black matrix.

Next, a color filter provided with a black matrix was fabricated. Namely, the above black-matrix-forming composition was coated as a first color by a roll coater on a glass substrate, which had been subjected to surface treatment with the silane coupling agent, to a wet thickness of 5 µm, followed by predrying at 60°C for 5 minutes. Thereafter, a photomask having a grid pattern thereon was brought into close contact with the thus-coated glass substrate, followed by exposure at 400 mJ/cm² under a 250 W extra-high pressure mercury lamp. Unexposed portions were then washed away with a developer which contained isopropyl alcohol, toluene and ethyl acetate as principal components. After rinsed with isopropyl alcohol, the coating layer was dried by dry air so that a grid-shaped black matrix having a line width of 50 µm was obtained.

On the glass substrate with the grid-shaped black matrix formed thereon as described above, the R, G and B inks were uniformly coated one ink after another as second, third and fourth colors, respectively, by a roll coater as in the case of the black-matrix-forming composition so that the three colors of R, G and B are cyclically arranged in the resulting black matrix grid and no regions of the same color are located adjacent to each other. Using photomasks for R, G and B, exposure was conducted to form an R, G and B mosaic pattern so that an R, G and B color filter provided with the black matrix was obtained.

Following a conventional method, an oriented film for LCD was formed on the color filter substrate obtained as described above. Rubbing, printing of seals, and formation of transfer electrodes were then conducted. On the side, TFT elements and an oriented film for LCD were formed on an array substrate. Rubbing was conducted and a spacer was then spread. The array substrate and the color filter substrate were bonded together. Injection of a liquid crystal, sealing and bonding of polarizers were then conducted, whereby a color LC panel was obtained. Through a module assembly step in which an integrated driver circuit and an integrated control circuit were connected to the color LC panel and an illuminating backlight or the like is mounted, an LC color display was fabricated.

Since the individual R, G and B colors were isolated from each other by the black matrix, the thus-obtained LC color display was able to form a vivid image with good color reproducibility without overlapping of the individual colors.

Example 2

Similarly to Example 1, an LC display having a color filter provided with a black matrix was fabricated. Specifically, 35 parts of the compound-oxide black pigment "BK-8" obtained in Synthesis Example 8 were used instead of "BK-1". By a dispersion mixer, a black-matrix-forming UV-curing composition was prepared in accordance with the following formula:

	Parts
"BK-8"	35
Polyurethane acrylate resin varnish	25
Trimethylolpropane triacrylate	8
Neopentyl glycol diacrylate	4
2-Hydroxy-2-methylpropylphenone	1.8
2,2-Diethoxyacetophenone	0.9
Isopropyl alcohol	13.7
Toluene	6.8
Ethyl acetate	4.8

50

The above black-matrix-forming composition was coated to a wet thickness of 3 µm by a roll coater on a surface-treated glass substrate, followed by exposure and insolubilization. The optical density of the resultant coating film was 2.9. The coating film had high surface resistance so that sufficient electrical insulating property was exhibited. It also had high light shielding property. It therefore demonstrated to have excellent performance as a black matrix.

Next, a color filter provided with a black matrix was fabricated. Namely, the above black-matrix-forming composition was coated by a roll coater on a surface-treated glass substrate to give a wet thickness of 3 µm. Subsequent to predrying, a photomask was applied in close contact with the thus-coated glass substrate. Under an extra-high pressure mercury lamp, the coating layer was subjected to exposure and insolubilization. Unexposed portions were then washed

away. The thus-exposed coating layer was rinsed and dried, whereby a grid-shaped black matrix having a line width of 50 µm was obtained.

Using the R, G and B inks and B, G and R photomasks employed in Example 1, a color filter having an R, G and B mosaic pattern was next obtained. Thereafter, an LC color display was fabricated in a usual manner. Since the individual R, G and B colors were isolated from each other by the black matrix, the LC color display was able to form a vivid image having high color purity, high contrast and excellent luminance.

Example 3

Similarly to Example 1, an LC display having a color filter provided with a black matrix was fabricated. Specifically, the compound-oxide black pigment "BK-10", which had been obtained in Synthesis Example 10 and surface-treated with the siliceous material, was used instead of "BK-1" employed in Example 1. Using the pigment, polyurethane acrylate resin varnish, polyacrylate monomers, photopolymerization catalyst and solvents in the same proportions, a black-matrix-forming UV-curing composition was prepared by a dispersion mixer.

The above black-matrix-forming composition was coated to a wet thickness of 3 µm by a roll coater on a surface-treated glass substrate, followed by exposure and insolubilization. The optical density of the resultant coating film was 2.6. The coating film had high surface resistance so that sufficient electrical insulating property was exhibited. It also had high light shielding property. It therefore demonstrated to have excellent performance as a black matrix.

Next, a color filter provided with a black matrix was fabricated. Namely, the above black-matrix-forming composition was coated by a roll coater on a surface-treated glass substrate to give a wet thickness of 3 µm. Subsequent to pre-drying, a photomask was applied in close contact with the thus-coated glass substrate. Under an extra-high pressure mercury lamp, the coating layer was subjected to exposure and insolubilization. Unexposed portions were then washed away. The thus-exposed coating layer was rinsed and dried, whereby a grid-shaped black matrix having a line width of 50 µm was obtained. Using the R, G and B inks and B, G and R photomasks employed in Example 1, a color filter having an R, G and B mosaic pattern was next obtained. Thereafter, an LC color display was fabricated in a usual manner. Since the individual R, G and B colors were isolated from each other by the black matrix, the LC color display was able to form a vivid image having high color purity, high contrast and excellent luminance.

Example 4

Similarly to Example 1, an LC display having a color filter provided with a black matrix was fabricated. Specifically, the compound-oxide black pigment "BK-14", which had been obtained in Synthesis Example 14 and surface-treated with the resin, was used instead of "BK-1" employed in Example 1. Using the pigment, polyurethane acrylate resin varnish, polyacrylate monomers, photopolymerization catalyst and solvents in the same proportions, a black-matrix-forming UV-curing composition was prepared by a dispersion mixer.

The above black-matrix-forming composition was coated to a wet thickness of 5 µm by a roll coater on a surface-treated glass substrate. Subsequent to pre-drying, exposure and insolubilization were conducted. The optical density of the resultant coating film was 3.1. The coating film had high surface resistance so that sufficient electrical insulating property was exhibited. It also had high light shielding property. It therefore demonstrated to have excellent performance as a black matrix.

Next, a color filter provided with a black matrix was fabricated. Namely, the above black-matrix-forming composition was coated by a roll coater on a surface-treated glass substrate to give a wet thickness of 5 µm. Subsequent to pre-drying, a photomask was applied in close contact with the thus-coated glass substrate. Under an extra-high pressure mercury lamp, the coating layer was subjected to exposure and insolubilization. Unexposed portions were then washed away. The thus-exposed coating layer was rinsed and dried, whereby a grid-shaped black matrix having a line width of 50 µm was obtained.

Using the R, G and B inks and B, G and R photomasks employed in Example 1, a color filter having an R, G and B mosaic pattern was next obtained. Thereafter, an LC color display was fabricated in a usual manner. Since the individual R, G and B colors were isolated from each other by the black matrix, the LC color display was able to form a vivid image having high color purity, high contrast and excellent luminance.

Example 5

Similarly to Example 1, an LC display having a color filter provided with a black matrix was fabricated. Specifically, the compound-oxide black pigment "BK-15", which had been obtained in Synthesis Example 15 and surface-treated with the resin, was used instead of "BK-1" employed in Example 1. Using the pigment, polyurethane acrylate resin varnish, polyacrylate monomers, photopolymerization catalyst and solvents in the same proportions, a black-matrix-forming UV-curing composition was prepared by a dispersion mixer.

The above black-matrix-forming composition was coated to a wet thickness of 5 µm by a roll coater on a surface-treated glass substrate. Subsequent to pre-drying, exposure and insolubilization were conducted. The optical density of the resultant coating film was 2.9. The coating film had high surface resistance so that sufficient electrical insulating property was exhibited. It also had high light shielding property. It therefore demonstrated to have excellent performance as a black matrix.

Next, a color filter provided with a black matrix was fabricated. Namely, the above black-matrix-forming composition was coated by a roll coater on a surface-treated glass substrate to give a wet thickness of 5 µm. Subsequent to predrying, a photomask was applied in close contact with the thus-coated glass substrate. Under an extra-high pressure mercury lamp, the coating layer was subjected to exposure and insolubilization. Unexposed portions were then washed away. The thus-exposed coating layer was rinsed and dried, whereby a grid-shaped black matrix having a line width of 50 µm was obtained.

Using the R, G and B inks and B, G and R photomasks employed in Example 1, a color filter having an R, G and B mosaic pattern was next obtained. Thereafter, an LC color display was fabricated in a usual manner. Since the individual R, G and B colors were isolated from each other by the black matrix, the LC color display was able to form a vivid image having high color purity, high contrast and excellent luminance.

Example 6

Similarly to Example 1, an LC display having a color filter provided with a black matrix was fabricated. Specifically, 20 parts of the compound-oxide black pigment "BK-10", which had been obtained in Synthesis Example 10, and 10 parts of a below-described carbon black pigment, which had been surface-treated with a siliceous material, were used instead of "BK-1" employed in Example 1. By a dispersion mixer, a black-matrix-forming UV-curing composition was prepared in accordance with the following formula:

	Parts
	"BK-10"
20	20
	Surface-treated carbon black pigment
30	10
	Polyurethane acrylate resin varnish
35	25
	Trimethylolpropane triacrylate
40	8
	Neopentyl glycol diacrylate
	4
	2-Hydroxy-2-methylpropylphenone
	1.8
	2,2-Diethoxyacetophenone
	0.9
	Isopropyl alcohol
	16.3
	Toluene
	8
	Ethyl acetate
	6

The above black-matrix-forming composition was coated by a roll coater on a surface-treated glass substrate. Subsequent to predrying, exposure and insolubilization were conducted. The optical density of the resultant coating film was 3.5. The coating film had high surface resistance so that sufficient electrical insulating property was exhibited. It also had high light shielding property. It therefore demonstrated to have excellent performance as a black matrix.

Next, a color filter provided with a black matrix was fabricated. Namely, the above black-matrix-forming composition was coated by a roll coater on a surface-treated glass substrate. Subsequent to predrying, a photomask was applied in close contact with the thus-coated glass substrate, followed by exposure and insolubilization. Unexposed portions were then washed away. The thus-exposed coating layer was rinsed and dried, whereby a grid-shaped black matrix having a line width of 50 µm was obtained. Using the R, G and B inks and B, G and R photomasks employed in Example 1, similar operations were conducted so that a color filter having an R, G and B mosaic pattern was obtained.

Then, an LC color display was fabricated in a usual manner.

Since the individual R, G and B colors were isolated from each other by a black matrix, the above-obtained LC color display was able to form a vivid image having high color purity, high contrast and excellent luminance.

The surface-treated carbon black pigment employed as described above had been obtained as in Synthesis Example 3 by subjecting a carbon black pigment (C.I. Pigment Black 7) to surface treatment with a siliceous material in an amount of about 20% based on the pigment.

Example 7

To fabricate an LC display having a color filter provided with a black matrix, 30 parts of the fine particulate, compound-oxide black pigment "BK-4" obtained in Synthesis Example 4 were added to and mixed with a photosensitive resin varnish which was composed of 23 parts of a methacrylate ester-methacrylic acid copolymer resin of the alkaline development type, 10 parts of pentaerythritol triacrylate, 5 parts of diethylene glycol diacrylate and 30 parts of propylene glycol monomethyl ether acetate. The pigment was dispersed in a ball mill. Further, 5 parts of a photopolymerization initiator were added and mixed, whereby a black-matrix-forming UV-curing composition was prepared.

The above black-matrix-forming composition was coated by a roll coater to a wet thickness of 3 µm on a surface-treated glass substrate. Subsequent to pre-drying, exposure and insolubilization were conducted. The optical density of the resultant coating film was 2.8. The coating film had high surface resistance so that sufficient electrical insulating property was exhibited. It also had high light shielding property. It therefore demonstrated to have excellent performance as a black matrix.

The black-matrix-forming UV-curing composition was coated to a wet thickness of 3 µm on a surface-treated glass substrate by a roll coater. Next, pre-drying was conducted at 60°C for 5 minutes. A photomask having a grid pattern therein was then brought into close contact with the thus-coated glass substrate. Under a 250 W extra-high pressure mercury lamp, exposure was conducted at a light quantity of 400 mJ/cm² to insolubilize the coating layer. Unexposed portions were then washed away with a developer which contained sodium carbonate as a principal component in a dilute aqueous solution of isopropyl alcohol. The thus-washed coating layer was dried at 60°C, whereby a grid-shaped pattern was obtained.

The pigments BL-1, G-1 and R-1 employed in Example 1 were then separately added to and mixed with portions of the above-described photosensitive resin varnish. Using ball mills, the pigments were separately dispersed and a photopolymerization initiator was then added and mixed, so that UV-curing R, G and B inks were prepared. To form an R, G and B pattern similar to that obtained in Example 1, operations were conducted as described above, using the R, G and B inks and B, G and R photomasks, a color filter having an R, G and B mosaic pattern was obtained. An LC color display was then fabricated in a usual manner. Since the individual R, G and B colors were isolated from each other by the black matrix, the LC color display so obtained was able to form a vivid image having high color purity, high contrast and excellent luminance.

Example 8

To fabricate an LC display having a color filter which was provided with a black matrix, pigments, that is, the compound-oxide black pigment "BK-2" obtained in Synthesis Example 2 and the pigments "R-1", "G-1" and "BL-1" of the individual colors used in Example 1 were separately dispersed by a three-roll mill in portions of a photosensitive aromatic polyimide resin varnish containing a photosensitizer in accordance with the below-described formula, whereby photosensitive compositions of the four colors were prepared for a color filter.

Component	Bk	R	G	B
Compound-oxide black pigment "BK-2"	20	-	-	-
Red pigment "R-1" (C.I. Pigment Red 149)	-	10	-	-
Green pigment "G-1" (C.I. Pigment Green 36)	-	-	10	-
Blue pigment "BL-1" (C.I. Pigment Blue 15)	-	-	-	10
Photosensitive polyimide resin varnish	50	50	50	50
N-Methyl-2-pyrrolidone	30	40	40	40
Total	100	100	100	100

To investigate performance as a black matrix, a glass plate which had been treated with a silane coupling agent was mounted on a spinner and the above-described black-matrix-forming composition according to the present invention was spin-coated. The spin coating was conducted first at 1,000 rpm for 5 seconds and then at 2,000 rpm for 5 seconds.

Pre-baking was next conducted at 65°C for 30 seconds. Using an extra-high pressure mercury lamp, full-surface exposure was conducted at a light quantity of 900 mJ/cm². The coating layer was subjected to post-baking at 200°C for 30 minutes and then at 300°C for 60 minutes. The blackness of the resultant coating film was measured by a Macbeth

densitometer. A value of 2.9 was indicated. The glass substrate with the coating film formed thereon was placed in front of a fluorescent lamp to investigate its light shielding property. Light from the lamp was completely shielded, thereby demonstrating excellent performance as a black matrix.

Next, a color filter provided with a black matrix was fabricated. A glass plate which had been treated with the silane coupling agent was mounted on a spinner and the above-described black-matrix-forming composition according to the present invention was spin-coated. The spin coating was conducted first at 1,000 rpm for 5 seconds and then at 2,000 rpm for 5 seconds. Pre-baking was next conducted at 65°C for 30 seconds. A photomask having a grid pattern was applied in close contact with the thus-coated glass plate. Using an extra-high pressure mercury lamp, full-surface exposure was conducted at a light quantity of 900 mJ/cm². The resulting coating layer was developed with a specially-prepared developer and then washed with a specially-prepared rinse, followed by post-baking at 200°C for 30 minutes and then at 300°C for 60 minutes. A glass substrate provided with a grid-shaped black matrix pattern having a line width of 20 µm was obtained.

Using a blue color composition as a second color, a green color composition as a third color and a red color composition as a fourth color, operations similar to those conducted with the black matrix composition according to the present invention were repeated three times, so that a color filter having a mosaic pattern was obtained. Next, a LC color display was fabricated in a usual manner. As the individual R, G and B colors did not overlap, the LC color display was excellent in color-light separability and luminance and was able to form a very vivid image.

Example 9

A LC display having a color filter provided with a black matrix was fabricated in a similar manner as in Example 8. In place of "BK-2" used in Example 8, 30 parts of the surface-treated, compound-oxide black pigment "BK-11" obtained in Synthesis Example 11 were dispersed in a mixture which consisted of 45 parts of a photosensitive polyimide resin varnish containing a photosensitizer and 25 parts of N-methyl-2-pyrrolidone.

The above black-matrix-forming composition according to the present invention was spin-coated on a surface-treated glass substrate. The coating layer was subjected to pre-baking, exposure and post-baking. The optical density of the resultant coating film was 2.8. The coating film had high surface resistance so that sufficient electrical insulating property was exhibited. It also had high light shielding property. It therefore demonstrated to have excellent performance as a black matrix.

Next, a color filter provided with a black matrix was fabricated. Specifically, the black-matrix-forming composition according to the present invention was spin-coated on a surface-treated glass substrate. Subsequent to pre-baking, a photomask was applied in close contact with the thus-coated glass substrate, followed by exposure and insolubilization, development and washing, and post-baking. A glass substrate provided with a grid-shaped black matrix pattern having a line width of 20 µm was obtained. Using the R, G and B colored compositions employed in Example 8, similar operations were conducted so that a color filter provided with an R, G and B mosaic pattern was obtained.

An LC color display was then fabricated in a usual manner. Since the individual R, G and B colors were isolated from each other by the black matrix, the color display so obtained was able to form a vivid image having high color purity, high contrast and excellent luminance.

Example 10

Twenty-five parts of the compound-oxide black pigment "BK-5", which had been obtained in Synthesis Example 5, were added to and mixed with a photosensitive resin varnish which was composed of 10 parts of the styrene-methacrylate ester-methacrylic acid copolymer resin of the alkaline development type, 5 parts of pentaerythritol triacrylate, 2 parts of diethylene glycol diacrylate and 56 parts of propylene glycol monomethyl ether acetate. The pigment was dispersed in a ball mill. Further, 2 parts of the photopolymerization initiator were added and mixed, whereby a black-matrix-forming UV-curing composition according to the present invention was prepared.

The above black-matrix-forming composition according to the present invention was spin-coated to a wet thickness of 3 µm on a surface-treated glass substrate, first at 200 rpm for 30 seconds and then at 1,200 rpm for 5 seconds. The coating layer was subjected to pre-baking, exposure and post-baking. The optical density of the resultant coating film was 3.2. The coating film had high surface resistance so that sufficient electrical insulating property was exhibited. It also had high light shielding property. It therefore demonstrated to have excellent performance as a black matrix.

A surface-treated glass substrate was mounted on a spin coater, and the above-described black-matrix-forming UV-curing composition was spin-coated to a wet thickness of 3 µm first at 200 rpm for 5 seconds and then at 1,200 rpm for 5 seconds. After pre-baking was conducted at 60°C for 5 minutes, a photomask having a grid pattern was applied in close contact with the thus-coated glass substrate. Using a 250 W extra-high pressure mercury lamp, exposure was conducted at a light quantity of 400 mJ/cm² to insolubilize the coating layer. Unexposed portions were then washed away with a developer which contained sodium carbonate as a principal component in a dilute aqueous solution of isopropyl alcohol. The resulting coating layer was dried at 60°C, whereby a grid pattern was obtained.

The pigments "BL-1", "G-1" and "R-1" employed in Example 1 were then separately added to and mixed with portions of the above-described photosensitive resin varnish. Using ball mills, the pigments were separately dispersed and the photopolymerization initiator was then added and mixed, so that UV-curing R, G and B inks were prepared. To form an R, G and B pattern similar to that obtained in Example 1, operations were conducted as described above, using the R, G and B inks and B, G and R photomasks, a color filter having an R, G and B mosaic pattern was obtained. An LC color display was then fabricated in a usual manner. Since the individual R, G and B colors were isolated from each other by the black matrix, the color display so obtained was able to form a vivid image having high color purity, high contrast and excellent luminance.

10 Example 11

To fabricate an LC display having a color filter which was provided with a black matrix, pigments, that is, the compound-oxide black pigment "BK-13" obtained in Synthesis Example 13 and surface-treated with the resin, C.I. Pigment Blue 15 (BL-2) and C.I. Pigment Violet 23 (V-1), and the red pigment "R-1", the green pigment "G-1" and the blue pigment "BL-1" employed in Example 1 were proportioned in accordance with the following formula and then dispersed, whereby black, R, G and B inks were prepared for offset lithographic printing.

Component	Bk	R	G	B
Surface-treated, compound-oxide black pigment "BK-13"	25	-	-	-
Blue pigment "BL-2"	5	-	-	-
Violet pigment "V-1"	10	-	-	-
Red pigment "R-1" (C.I. Pigment Red 149)	-	30	-	-
Green pigment "G-1" (C.I. Pigment Green 36)	-	-	40	-
Blue pigment "BL-1" (C.I. Pigment Blue 15)	-	-	-	20
Mixed varnish for offset lithographic inks	50	60	50	70
Drier	1	1	1	1
Ink solvent	9	9	9	9
Total	100	100	100	100

The above mixed varnish for offset lithographic inks has been obtained by using a rosin-modified phenol resin and a drying-oil-modified isophthalic alkyd resin as principal components and adding thereto an ink solvent and aluminum chelate.

To investigate performance as a black matrix, solid printing was conducted with the above black-matrix-forming composition by using an offset press. The optical density of the resultant coating film was 3.0. The coating film had high surface resistance so that sufficient electrical insulating property was exhibited. It also had high light shielding property. It therefore demonstrated to have excellent performance as a black matrix.

Next, a color filter provided with a black matrix was fabricated. Specifically, using the R, G and B inks, an R, G and B pixel pattern in the form of stripes having a line width of 200 µm was formed by a four-color offset press. Further, the black-matrix-forming composition was printed in a pattern such that the black-matrix-forming composition filled up both top and bottom sides and left and right sides of each of the R, G and B stripes, whereby the individual R, G and B pixels were completely isolated by the black matrix. An LC color display was then fabricated in a usual manner.

Since the individual R, G and B colors were isolated from each other by the black matrix, the LC color display so obtained was able to form a vivid image having high color purity, high contrast and excellent luminance.

Example 12

To fabricate an LC display having a color filter provided with a black matrix as in Example 11, a black-matrix-forming composition for offset lithographic printing was prepared using the compound-oxide black pigment "BK-10", which had been obtained in Synthesis Example 10 and surface-treated with the siliceous material, in place of "BK-11".

Solid printing was conducted with the above black-matrix-forming composition by using an offset press. The optical density of the resultant coating film was 2.7. The coating film had high surface resistance so that sufficient electrical

insulating property was exhibited. It also had high light shielding property. It therefore demonstrated to have excellent performance as a black matrix.

Next, a color filter provided with a black matrix was fabricated. Specifically, using the above-described black-matrix-forming composition in combination with the R, G and B inks employed in Example 11, an R, G and B pixel pattern provided with a black matrix was formed by a four-color offset press. An LC color display was then fabricated in a usual manner. Since the individual R, G and B colors were isolated from each other by the black matrix, the LC color display so obtained was able to form a vivid image having high color purity, high contrast and excellent luminance.

Example 13

To fabricate an LC display having a color filter provided with a black matrix as in Example 11, a black-matrix-forming composition for offset lithographic printing was prepared using the compound-oxide black pigment "BK-3", which had been obtained in Synthesis Example 3, in place of "BK-11".

Solid printing was conducted with the above black-matrix-forming composition by using an offset press. The optical density of the resultant coating film was 2.8. The coating film had high surface resistance so that sufficient electrical insulating property was exhibited. It also had high light shielding property. It therefore demonstrated to have excellent performance as a black matrix.

Next, a color filter provided with a black matrix was fabricated. Specifically, using the above-described black-matrix-forming composition in combination with the R, G and B inks employed in Example 11, an R, G and B pixel pattern provided with a black matrix was formed by a four-color offset press. An LC color display was then fabricated in a usual manner. Since the individual R, G and B colors were isolated from each other by the black matrix, the LC color display so obtained was able to form a vivid image having high color purity, high contrast and excellent luminance.

Example 14

To fabricate an LC display having a color filter provided with a black matrix as in Example 12, 6 parts of C.I. Pigment Blue 28 ("BL-2") obtained in Synthesis Example 16, 24 parts of C.I. Pigment Green 26 ("GR-2") and 30 parts of C.I. Pigment Brown 33 ("BR-1") were mixed, followed by the further addition of 30 parts of a mixed varnish for offset lithographic inks, 1 part of drier and 9 parts of ink solvent. The pigments were dispersed using a three-roll mill, whereby a black-matrix-forming composition for offset lithographic printing was prepared.

Solid printing was conducted with the above black-matrix-forming composition by using an offset press. The blackness of the resultant coating film was measured by a Macbeth densitometer. A value of 2.9 was indicated. The print was placed in front of a fluorescent lamp to investigate its light shielding property. Light from the lamp was completely shielded, thereby demonstrating excellent performance as a black matrix.

A color filter provided with a black matrix was fabricated. Specifically, using the above-described black-matrix-forming composition in combination with the R, G and B inks employed in Example 11, an R, G and B pixel pattern provided with a black matrix was formed by a four-color offset press.

An LC color display was then fabricated in a usual manner. Since the individual R, G and B colors were isolated from each other by the black matrix, the LC color display so obtained was able to form a vivid image having high color purity, high contrast and excellent luminance.

Example 15

To fabricate a display panel provided with a black matrix for use in a plasma display panel, 36 parts of the compound-oxide black pigment "BK-1" obtained in Synthesis Example 1 and 20 parts of a low m.p. glass frit were mixed with 35 parts of a mixed varnish for screen printing inks and 9 parts of ink solvent. The resulting mixture was kneaded in a three-roll mill to thoroughly disperse the pigment, whereby a black-matrix-forming composition was obtained. The mixed varnish for screen printing inks was composed of ethylhydroxyethylcellulose, the pentaerythritol ester of rosin, a petroleum-base solvent and cellosolve as principal components.

To investigate performance as a black matrix for a display panel of a plasma display, the above black-matrix-forming composition was coated to a wet thickness of 3 µm by a wire bar coater on a glass substrate over the entire surface thereof. The coating layer was dried at 200°C and in a baking furnace, was then baked at 550°C for 1 hour in air to burn off organic components. The optical density of the black coating film so obtained was 3.2. The coating film had high light shielding property and also had excellent adhesion to the glass substrate. It therefore demonstrated to have excellent performance as a black matrix.

Next, a display panel provided with a black matrix for use in a plasma display panel was fabricated. Specifically, using the above black-matrix-forming composition, a grid pattern was printed on a front glass substrate by a screen printing machine. The coating layer was dried at 200°C and in a baking furnace, was then baked at 550°C for 1 hour in air to burn off organic components, whereby a black matrix was formed. Formed next were transparent electrodes,

metal electrodes, a transparent dielectric layer, stripe partitions, seal layers, and a magnesium oxide layer. Formed on a rear glass substrate were data electrodes, a white dielectric layer, stripe partitions, blue, green and red phosphor layers, and seal layers. The thus-formed front glass substrate and rear glass substrate were assembled. Sealing, evacuation and gas filling steps were then performed. The assembly so obtained was connected to a circuit unit so that a display panel for a color plasma display was fabricated.

Individual luminescent colors from the blue, green and red phosphors appear on the front glass substrate in such a way that they are isolated from each other by the grid-shaped black matrix. The thus-obtained display panel for the color plasma display can therefore form a vivid image having high color purity and contrast and excellent luminance.

10 Example 16

To fabricate a display panel provided with a black matrix for use in a plasma display, 40 parts of the black pigment "BK-9" obtained in Synthesis Example 9 and 10 parts of low m.p. glass frit were, as in Example 1, added to and mixed with a photosensitive resin varnish which was composed of 20 parts of a methacrylate ester-methacrylic acid copolymer resin of the alkaline development type, 7 parts of pentaerythritol triacrylate, 3 parts of diethylene glycol diacrylate and 18 parts of propylene glycol monomethyl ether acetate. The pigment was dispersed in a ball mill. Further, 2 parts of a photopolymerization initiator were added and mixed, whereby a black-matrix-forming UV-curing composition was prepared.

The black-matrix-forming UV-curing composition was coated to a wet thickness of 3 µm on a front glass substrate by a roll coater. Next, predrying was conducted at 60°C for 5 minutes. A photomask having a grid pattern therein was then brought into close contact with the thus-coated glass substrate. Under a 250 W extra-high pressure mercury lamp, exposure was conducted at a light quantity of 400 mJ/cm² to insolubilize the coating layer. Unexposed portions were then washed away with a developer which contained sodium carbonate as a principal component in a dilute aqueous solution of isopropyl alcohol. The thus-washed coating layer was dried at 60°C, whereby a grid-shaped pattern was obtained. The coating layer was heated at 200°C and in a baking furnace, was then baked at 550°C for 1 hour in air to burn off organic components, whereby a black matrix was formed. In a similar manner to Example 1, a display panel for a color plasma display was fabricated.

Individual luminescent colors from the blue, green and red phosphors appear on the front glass substrate in such a way that they are isolated from each other by the grid-shaped black matrix. The thus-obtained display panel for the color plasma display can therefore form a vivid image having high color purity and contrast and excellent luminance.

Example 17

To fabricate a display panel provided with a black matrix for use in a plasma display, 25 parts of the black pigment "BK-12" obtained in Synthesis Example 12 and 5 parts of low m.p. glass frit were, as in Example 1, added to and mixed with a photosensitive resin varnish which was composed of 10 parts of a styrene-methacrylate ester-methacrylic acid copolymer resin of the alkaline development type, 5 parts of pentaerythritol triacrylate, 3 parts of diethylene glycol diacrylate and 50 parts of propylene glycol monomethyl ether acetate. The pigment was dispersed in a ball mill. Further, 2 parts of a photopolymerization initiator were added and mixed, whereby a black-matrix-forming UV-curing composition was prepared.

A front glass substrate was mounted on a spin coater, and the above-described black-matrix-forming UV-curing composition was spin-coated to a wet thickness of 3 µm first at 200 rpm for 5 seconds and then at 1,200 rpm for 5 seconds. Next, the coating layer was subjected to predrying at 60°C for 5 minutes. After that, a photomask having a grid pattern was applied in close contact with the thus-coated glass substrate. Using a 250 W extra-high pressure mercury lamp, exposure was conducted at a light quantity of 400 mJ/cm² to insolubilize the coating layer. Unexposed portions were then washed away with a developer which contained sodium carbonate as a principal component in a dilute aqueous solution of isopropyl alcohol. The resulting coating layer was dried at 60°C, whereby a grid pattern was obtained. The coating layer was heated at 200°C and in a baking furnace, was then baked at 550°C for 1 hour in air to burn off organic components, whereby a black matrix was formed. In a similar manner to Example 1, a display panel for a color plasma display was fabricated.

Individual luminescent colors from the blue, green and red phosphors appear on the front glass substrate in such a way that they are isolated from each other by the grid-shaped black matrix. The thus-obtained display panel for the color plasma display can therefore form a vivid image having high color purity and contrast and excellent luminance.

It is to be noted that display panels having excellent black matrices and suited for use in color CD displays or color plasma displays can be obtained by using, instead of the compound-oxide black pigments employed in Examples 1-17, other compound-oxide black pigments and following the procedures of these Examples.

Claims

1. A composition for a black matrix, said composition being composed of a black pigment and a binder for said pigment, wherein said black pigment is a compound-oxide black pigment comprising at least two metal oxides and having a spinel or inverse-spinel crystalline structure.
- 5 2. The composition according to claim 1, wherein said compound-oxide black pigment is a compound oxide composed, as principal metal components, of at least two metals selected from the group consisting of copper, chromium, iron, manganese, cobalt, aluminum, nickel, zinc, antimony, titanium and barium.
- 10 3. The composition according to claim 1, wherein said compound-oxide black pigment is at least one compound-oxide black pigment selected from the group consisting of compound-oxide black pigments composed of copper and chromium as principal metal components, compound-oxide black pigments composed of copper and manganese as principal metal components, compound-oxide black pigments composed of copper, iron and manganese as principal metal components, compound-oxide black pigments composed of cobalt, chromium and iron as principal metal components, compound-oxide black pigments composed of cobalt, chromium, iron and manganese as principal metal components and compound-oxide black pigments composed of cobalt, nickel, chromium and iron; or a black or dark-colored mixture of at least two pigments selected from the group consisting of brown, green and blue compound-oxide pigments and all said compound-oxide black pigments.
- 15 4. The composition according to claim 1, wherein said compound-oxide black pigment has been surface-treated with at least one coating material selected from the group consisting of silicon oxide or vitreous inorganic materials, hardenable polymers, and polymers substantially insoluble in a medium.
- 20 5. The composition according to claim 1, wherein said binder is a mixture of an organic binder and a low m.p. glass frit.
- 25 6. A process for the formation of a black matrix on a substrate from a composition containing a black pigment, wherein said black pigment is a compound-oxide black pigment comprising at least two metal oxides and having a spinel or inverse-spinel crystalline structure.
- 30 7. The process according to claim 6, wherein said substrate is a substrate for a color filter of a color LC display.
- 35 8. The process according to claim 6, wherein said substrate is a substrate for a display panel of a luminescent flat panel display.
- 40 9. The process according to any one of claims 6-8, which comprises forming a black matrix on said substrate with the composition defined in claim 5, and heating said black matrix at 450-900°C to burn off said organic binder and to fuse said low m.p. glass frit, whereby said compound-oxide black pigment in said composition is fixed on said substrate.
- 45 10. An article comprising a substrate and a black matrix formed from a composition, which contains a black pigment, and provided on said substrate, wherein said black pigment is a compound-oxide black pigment comprising at least two metal oxides and having a spinel or inverse-spinel crystalline structure.
11. The article according to claim 10, which is a color LC display.
12. The article according to claim 10, which is a luminescent flat-panel display.
- 50 13. The article according to any one of claims 10-12, wherein said compound-oxide black pigment has been fixed on said substrate with a low m.p. vitreous binder.



EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	PATENT ABSTRACTS OF JAPAN vol. 95, no. 001 & JP-A-07 027912 (SUMITOMO CEMENT CO LTD), 31 January 1995, * abstract * * column 3, line 43 - line 48 *	1-4, 6-8, 10, 11	G02F1/1335
Y	---	5, 9, 12, 13	
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 399 (P-1579), 26 July 1993 & JP-A-05 072523 (KOJUNDO CHEM LAB CO LTD), 26 March 1993, * abstract * * column 2, line 36 - line 37 *	1-3, 6-8, 10, 11	
Y	---	4, 5, 9, 12, 13	
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 320 (P-1558), 17 June 1993 & JP-A-05 034514 (FUJI PHOTO FILM CO LTD), 12 February 1993. * abstract *	1, 4, 6-8, 10, 11	TECHNICAL FIELDS SEARCHED (Int.Cl.)
Y	---	5, 9, 12, 13	G02F G02B
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 007 (P-1670), 7 January 1994 & JP-A-05 249455 (TOSHIBA CORP), 28 September 1993, * abstract *	1, 4, 6-8, 10, 11	
Y	---	5, 9, 12, 13	
		-/-	
The present search report has been drawn up for all claims			
Place of search	Date of compilation of the search	Examiner	
MUNICH	17 July 1996	Maaswinkel, A	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or after the filing date		
A : technological background	D : document cited in the application		
O : non-written disclosure	R : document cited for other reasons		
F : intermediate document	S : member of the same patent family, corresponding document		



EUROPEAN SEARCH REPORT

Application Number
EP 96 10 6302

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CLS)						
X	EP-A-0 481 827 (DAINIPPON PRINTING CO LTD) 22 April 1992 * page 2, line 40 - line 42 * * page 3, line 45 *	1,4,6-8, 10,11							
Y	---	5,9,12, 13							
Y	GB-A-2 072 364 (HITACHI LTD) 30 September 1981 * page 1, line 4 - line 9 * * page 1, line 113 - line 118; claims 1,4 *	12							
Y	EP-A-0 641 671 (SIGMAX LTD) 8 March 1995 * page 8, line 18 - page 9, line 30 *	4,5,9,13							

			TECHNICAL FIELDS SEARCHED (Int.CLS)						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>MUNICH</td> <td>17 July 1996</td> <td>Maaswinkel, A</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	MUNICH	17 July 1996	Maaswinkel, A
Place of search	Date of completion of the search	Examiner							
MUNICH	17 July 1996	Maaswinkel, A							
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document							
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document									

Japanese Patent Application Laid-open

Laid-open Number: Hei 8-34923

Laid-open Date: February 6, 1996

Application Number: Hei 6-169507

Filing Date: July 21, 1994

Applicant: Sekisui Chemical Co., Ltd.

[Title of the Invention] Black photosensitive resinous composition and method for preparing black matrix

[Abstract]

[Structure] A black photosensitive resinous composition characterized by comprising a photosensitive polymer, a dyeable polymer, a dispersant, a coloring pigment and a black dyestuff.

[Effect] At first, since a black dyestuff is combined as a light shielding agent, a coating property on a substrate is improved compared with the case of using only a pigment and thus a coating without any uneven coating distribution can be obtained; secondly, since the black dyestuff is used, a coating having a low coating pressure can be obtained at a same light shielding property compared with the case of using only a pigment, which is advantageous when introduced into a liquid crystalline module; and thirdly, since an amount of ultraviolet ray irradiated can be decreased, an

irradiation time and an electric amount consumed can be saved.

[Scope of Claims for Patent]

[Claim 1] A black photosensitive resinous composition characterized by comprising a photosensitive polymer, a dyeable polymer, a dispersant, a coloring pigment and a black dyestuff.

[Claim 2] A method for preparing a black matrix characterized in that a black photosensitive resinous composition containing a photosensitive polymer, a dyeable polymer, a dispersant, a coloring pigment and a black dyestuff is coated on a transparent substrate, exposing it through a mask having a desired pattern and developing it to obtain a pattern, and coloring the obtained pattern by a black dyestuff.

[Detailed Description of the Invention]

[0001]

[Field of the Invention Application]

The present invention relates to a black matrix for forming a color filter of a color liquid crystalline display device and a photosensitive coloring resinous composition used for preparing the black matrix.

[0002]

[Prior Art]

Conventionally, as a black matrix used in the color liquid crystalline display device, metallic deposited coatings of aluminum and chromium etc. However, pinholes may be easily produced in these

metallic deposited coatings, and furthermore there is a problem to produce a step between the black matrix part and other filter part.

[0003]

Thus, in order to solve such problems, a method to form a black matrix by means of an organic coating was proposed. For example, a resist having dispersed pigments which comprise combinations of carbon black with different multiple coloring pigments was disclosed Japanese Patent Application Laid-open No. Hei 4-63870. In the resist, a resist coating is formed on a transparent substrate by means of a spin coater method etc. similar to conventional coloring color resists, and then a pattern is formed by a photolithographic method.

[0004]

However, since the pigment is used as a coloring agent in the above-mentioned present invention, a concentration of the pigment should be increased for improving a light shielding property, thus a coating property is deteriorated and uneven coating distribution is easily produced when formed into a coating. Further, the pattern is formed by a photolithographic method in the above-mentioned present invention, but a light amount at a photoreacting site in the coating is decreased due to a light shielding property of a black matrix and thus a crosslinking efficiency is lowered. If a light amount necessary for photocrosslinking is not obtained, the

pattern is dissolved during development and thus peeled off. Further, if a photocrosslinking efficiency is lowered, an exposure amount necessary for forming a pattern of a color filter is increased, that is, a considerable exposure time is necessary. This tends to be eminent if the light shielding property of the black matrix is increased, that is if transparency is lowered, and thus such black color resist requires 3-10 times of exposure amount compared the coloring color resist. Conversely, if transparency is increased, the photocrosslinking efficiency is certainly improved, but the light shielding property is lowered, thus improvement in a contrast which is an object of a light shielding color resist is deteriorated.

[0005]

[Problem to be solved by the Invention]

A subject of the present invention is to provide a black photosensitive resinous composition by which a pigment density in a coating is lowered without varying a light shielding property and a coating property of the coating and by which a dispersing property of a pigment can be improved, and a method for forming a black matrix at a low exposure amount without lowering the light shielding property.

[0006]

[Means to solve the Problem]

The present inventors have studied eagerly about the above-mentioned subject, to find that a pigment density in a coating

is lowered without varying a light shielding property and a coating property of the coating and a dispersing property of a pigment can be improved by using not only a coloring pigment but also a black dyestuff combined, and that a black matrix can be formed at a low exposure amount without lowering the light shielding property when a coloring pigment and others are coated first to form a coating, exposed and then dyed with a black dyestuff, in the case of preparing the black matrix with using the composition, and to attain the present invention.

[0007]

That is, the present invention relates to a black photosensitive resinous composition characterized by comprising a photosensitive polymer, a dyeable polymer, a dispersant, a coloring pigment and a black dyestuff. Further, the present invention relates to a method for preparing a black matrix characterized in that a black photosensitive resinous composition containing a photosensitive polymer, a dyeable polymer, a dispersant, a coloring pigment and a black dyestuff is coated on a transparent substrate, exposing it through a mask having a desired pattern and developing it to obtain a pattern, and coloring the obtained pattern by a black dyestuff.

[0008]

The present invention will be illustrated in detail as follows.

[0009]

[A] black photosensitive resinous composition

The black photosensitive resinous composition according to the present invention contains a photosensitive polymer, a dyeable polymer, a dispersant, a coloring pigment and a black dyestuff. Respective components will be described in detail as follows.

[0010]

(1) photosensitive polymer

As the photosensitive polymers according to the present invention, combinations of binder resins and photocrosslinking agents can be used. The binder resins may be, for example, polyvinyl alcohol, polyvinyl pyrrolidone, acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate and polyacrylamide.

[0011]

As photocrosslinking agents, diazo compounds and azide compounds etc. are preferably used. The diazo compound in the present invention is referred to a compound having one, preferably two or more, diazo salt(s) in one molecule. Preferably, aromatic diazo compounds are used. Specific examples of the aromatic diazo compound include condensates of p-diazodiphenylamine, 2,5-dimethoxy-4-p-tolylmercaptobenzene diazonium, 2,5-dimethoxy-4-morpholinobenzene diazonium with formaldehyde, etc.

[0012]

The azide compound in the present invention is referred to a compound having one, preferably two or more, azide salt(s) in one molecule. The azide compound is used generally as a sulfonic acid or sulfonate form. Examples of the azide compounds include sodium 4,4-diazidestilbene-2,2'-disulfonate, 2,6-bis(4-azidebenzal)acetone 2-sulfonic acid, 2,6-bis(4-azidebenzal)acetone 2,2'-disulfonic acid, 2,6bis(4-azidebenzal)cyclohexanone-2-2'-disulfonic acid, 2,6bis(4-azidebenzal)methylcyclohexanone-2,2'-disulfonic acid, etc.

[0013]

A large amount of the diazo compound or the azide compound to be added is preferred from the viewpoint of crosslinking efficiency, but if it is too much, a dispersing property of the pigment is lowered. Therefore, it is preferable added in an amount of 1-30% by weight based on a binder resin (solid content). Since these photocrosslinking agents are rich in reactivity, they are preferably added to the binder resin immediately before its practical use. An amount of the photosensitive polymer contained in 100 parts by weight of the black photosensitive resinous composition is preferably 2-25 parts by weight. If it is less than 2 parts by weight, photosensitivity becomes low, and if it is above 25 parts by weight, viscosity is increased and thus a coating property on a substrate is lowered.

[0014]

(2) dyeable polymer

The dyeable polymer in the present invention is referred to a polymer which exhibits color by optical absorption of the dyeable molecules after a dyestuff molecules are adsorbed on a specific functional group contained in the polymer in the case of adding a suitable dyestuff (described below specifically). Dyeable polymers may be, for example, homopolymers and copolymers such as casein, glue, polyvinyl alcohol, polyvinyl pyrrolidone or polyacrylamide. Particularly, among of the above-mentioned ones, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylamide, 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate having also a property of the binder resin are preferable. An amount of the dyeable polymer contained in 100 parts by weight of the black photosensitive resinous composition is preferably 5-20 parts by weight. If it is less than 5 parts by weight, the effect of the present invention is hardly obtained, and if it is above 20 parts by weight, a coating property on a substrate is lowered.

[0015]

(3) dispersant

Examples of the dispersants include ionic surfactants, nonionic surfactants and various polymers, wherein the ionic surfactants include cationic surfactants, anionic surfactants and amphoteric surfactants.

[0016]

Examples of the cationic surfactants include aliphatic amines, quaternary ammonium salts and alkyl pyridinium salts; examples of the anionic surfactants include aliphatic acid salts, sulfuric esters, sulfonic salts and phosphoric esters; and examples of amphoteric surfactants include amino acid salts. Examples of the nonionic surfactants include polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene alkyl esters, sorbitan alkyl esters and polyoxyethylene sorbitan alkyl esters.

[0017]

Further, examples of the dispersants comprising polymers include alkyd resins, epoxy, epoxy esters, vinyl resins, butyral resins, polyurethane, acrylic resins, polyester resins, silicone resins and water-soluble resins etc. These dispersant may be used in admixture each other, or they can be used after dispersing alone and then adding other ones. For chemical stability, it is preferable to disperse the pigment first by means of a surfactant having a low molecular weight and thereafter add the polymer dispersant.

[0018]

An amount of the dispersant contained in 100 parts by weight of the black photosensitive resinous composition is preferably 0.5-40 parts by weight. If it is less than 0.5 parts by weight, a dispersing property of the pigment is bad, and if it is above 40 parts by weight, a coating property on a substrate is lowered.

[0019]

(4) coloring pigment

As coloring pigments, organic pigments are mainly used but inorganic pigments may be used, and both may be also used in together. Examples of organic pigments include azo lake type, insoluble azo type, condensed azo type, phthalocyanine type, quinacridone type, dioxazine type, isoindolinone type, anthraquinone type, perynone type, thioindigo type and perylene type. Example of inorganic pigments include carbon black, titanium oxide, Mlori blue, cobalt violet, manganese violet, ultramarine, Prussian blue, cobalt blue, cerulean blue and viridian. As to carbon black, it is preferably unused since it has a high light shielding property by itself and a long period is necessary for exposure of the photosensitive composition. In this case, the light shielding property can be kept by using the black dyestuff described below much.

[0020]

The above-mentioned coloring pigments may be used alone or in admixture. Further, it is preferably used by combining a pigment which is in a complementary relationship or by blackening falsely to exhibit black color by using the above coloring pigment. As examples of the complementary relationship, red and bluish green, violet and green, yellow and blue, etc. may be mentioned. An amount of the pigment contained in 100 parts by weight of the black photosensitive resinous composition is preferably 30 parts by

weight or less. If it is above 30 parts by weight, dispersing stability is deteriorated. Further, a ratio of the pigment to the above-mentioned dispersant is preferably 1:0.2-1:10. Since the photosensitive resinous composition according to the present invention has a dyestuff in addition to the coloring pigment, the amount of the coloring pigment added can be suppressed low and thus the dispersing property of the pigment can be improved.

[0021]

(5) dyestuff

The dyestuff used in the present invention is one which is adsorbed on the above-mentioned dyeable polymer and which exhibits black color when coated on a pattern obtained by exposing and developing the photosensitive resinous composition. Such black dyestuffs may be, for example, Direct Fast Black D which is a direct dyestuff, Acid Fast Black VLG which is an acidic dyestuff, Acid Black WA which is a 1:1 type metal complex dyestuff, Chromium Black P2B and Chromium Black T which are chromium dyestuffs, and Reactive Black B which is a reactive dyestuff.

[0022]

Examples of preferable combinations with dyeable polymers include a combination of casein or glue with Direct Fast Black D, a combination of polyvinyl alcohol or 2-hydroxyethyl methacrylate with Acid Fast Black VLG or Acid Fast Black WA, a combination of polyacrylamide with Chromium Black P2B or Chromium Black T, and

a combination of polyvinyl alcohol with Reactive Black B.

[0023]

An amount of the black dyestuff contained in 100 parts by weight of the black photosensitive resinous composition may be adjusted in order that a coating has a desired light shielding property, that is, may be adjusted appropriately according to an amount of the coloring pigment added; and it is preferably 1-20% by weight, particularly 3-10% by weight.

[0024]

[B] method for preparation of black matrix

A method for preparation of a black matrix of the present invention is illustrated as follows.

[0025]

(1) preparation of photosensitive resinous composition

The above-mentioned photosensitive polymer, dyeable polymer, dispersant and coloring pigment are dispersed in a solvent at a specified weight ratio. As solvents, water and organic solvents such as alcohol, benzene, toluene, cyclohexane, methyl ethyl ketone, acetone and ethyl cellosolve can be used. The dispersing may be carried out by general methods with using a pigment dispersing device such as a three-roll mill, a ball mill, a sand mill, a homogenizer and an ultrasonic dispersing device. The coloring compositions (coloring pigments or dispersions containing dispersed coloring pigments) may be used alone, but it may be toned

with multiple coloring compositions in order to exhibit good color characteristics.

[0026]

(2) coating of photosensitive resinous composition and forming of pattern

The photosensitive resinous composition obtained as described above is coated on a transparent substrate such as a glass substrate by a coating machine such as a spin coater and a roll coater, to form a coating. Herein, the coating is formed in such a thickness that transparency is higher than the objective one in due consideration of later dyeing of the coating. Specifically, the coating thickness is preferably 1.5-5 times of the objective transparency (which can be calculated from the Lambert-Beer law). In the photosensitive resinous composition according to the present invention, density of the coloring pigment can be suppressed low, so that viscosity becomes low and a coating property becomes good.

[0027]

Then, the thus formed photosensitive resinous coating is irradiated with ultra-violet ray through a mask having a specified pattern. The amount of exposure is about 200-2000 mJ/cm². In the case that carbon black is not used as the coloring pigment in the photosensitive resinous composition, the amount of exposure is about 400 mJ/cm², wherein exposure takes a very short period compared with the case of carbon black used.

[0028]

By developing the photosensitive resin exposed through the mask, the pattern is formed only on an exposed area and an area covered with the mask is removed. As developers, generally used developers may be employed: aqueous developers such as a dilute aqueous acetic acid solution and an aqueous malic acid solution, as well as alkaline developers such as an aqueous sodium carbonate solution and an aqueous potassium carbonate solution.

[0029]

(3) dyeing

The coating pattern obtained as described above is dyed by means of the black dyestuff. Dyeing may be carried out by a conventional method, and generally the substrate is dipped in the dyestuff. A dipping period may be adjusted such that the coating has a desired light shielding property, and specifically it is preferably 3-20 minutes, particularly 5-10 minutes.

[0030]

In the case that an acidic dyestuff is used as the dyestuff, it is preferable to carry out pH adjustment and temperature adjustment appropriately in due consideration of dyeing efficiency. pH is preferably 3-5 at which physical properties of a formed coating are not changed, and it is particularly about 4. Further, the temperature is preferably 20-50°C, particularly preferably 25-35°C. Examples of acids which can be used for pH adjustment include

acetic acid, citric acid, malic acid and tartaric acid. Examples of salts include ammonium sulfate, ammonium sulfonate and ammonium nitrate.

[0031]

The black matrix obtained as described above has a sufficient light shielding property due to the coloring pigment and dyestuff.

[0032]

[Action]

By using the photosensitive resinous composition according to the present invention, a concentration of a pigment in a coating can be suppressed low and a coating property of the coating can be improved without any uneven coating distribution. Further, by the method for preparation of the black matrix according to the present invention, transparency of the coating during exposure can be maintained high (that is, the light shielding property can be maintained low) and thus an amount of ultra-violet rays irradiated necessary for exposure can be decreased since the coating is dyed with a dyestuff after exposure to obtain a desired light shielding property.

[0033]

[Examples]

The present invention is illustrated in more detail with referring to examples as follows without being limited thereto.

[0034]

(Example 1)

In this Example, coating properties of a photosensitive resinous composition were tested as follows. An acidic dyestuff PC-Black 205D (made by Nippon Kayaku Co. Ltd.) was selected as a black pigment, and Fastogen Blue TGR (made by Dainippon Ink Co. Ltd.) and Fastogen Super Violet RVS (made by Dainippon Ink Co. Ltd.) were selected as a blue and violet pigments, respectively. They were dispersed in a sand mill at a blending ratio described hereinafter at 2500 rpm for 2 hours. Herein, 2 mmφ glass beads were used as media.

PC-Black 205D	5% by weight
Fastogen Blue TGR	6% by weight
Fastogen Super Violet RVS	4% by weight
polyoxyethylene alkylphenyl ether	5% by weight
water	80% by weight

Then, to 100 parts by weight of the above-mentioned coloring resinous composition, 45 parts by weight of a 10% aqueous 2-hydroxyethyl methacrylate solution was added and further 1 part by weight of p-diazodiphenylamine was added.

[0035]

A light shielding property and a coating property of the thus obtained black resinous composition were evaluated. A light shielding property was evaluated by determining transparency. The maximal transparency was 1.5% at a coating thickness of 0.8 μm for

visible light (700 nm). Further, a yield value is used as a typical numerical value expressing the coating property, wherein the yield value is an extrapolated shear stress value at a shear rate 0 by varying the shear rate of viscosity. If the value is high, uneven coating distribution is easily produced due to high thixotropy and a bad coating property.

[0036]

The yield value was determined by measuring viscosity with by using an E type viscometer (made by TOKIMEC Co. Ltd.) and Casson plot. As the result, the yield value was 10 mPa.

[0037]

(Comparative Example 1)

A black resinous composition was prepared similarly to Example 1, except that carbon black (MA 100, made by Mitsubishi Kasei Co. Ltd.) was used instead of the black dyestuff in the same amount. As to the obtained composition, a maximal transparency and an yield value were determined similarly to Example 1, which were 1.5% and 100 mPa respectively. If the yield value is higher in such case, a coating property becomes bad and uneven coating distribution is produced when coated on a substrate.

[0038]

As clear from results of Example 1 and Comparative Example 1, the black resinous composition prepared by using the dyestuff and the pigment has a very low yield value and a superior coating

property compared with the black resinous composition having the similar light shielding property with use of only pigment.

[0039]

(Example 2)

Three types of organic pigments (black: carbon black (MA 100, made by Mitsubishi Kasei Co. Ltd.), blue: phthalocyanine blue (Fastogen Blue TGR, made by Dainippon Ink Co. Ltd.) and violet: dioxazine violet (Fastogen Super Violet RVS, made by Dainippon Ink Co. Ltd.)) were dispersed in water at a blending ratio described below by using a nonionic surfactant, polyoxyethylene alkylphenyl ether.

organic pigment	20% by weight
polyoxyethylene alkylphenyl ether	5% by weight
water	75% by weight

To the obtained pigment dispersion, a 10% aqueous 2-hydroxyethyl methacrylate (HEMA) solution, polyoxyethylene alkylphenyl ether and water were added at such amounts to provide the following composition ratio.

pigment dispersion	8% by weight
polyoxyethylene alkylphenyl ether	2% by weight
HEMA	8% by weight
water	82% by weight

To the obtained respective coloring pastes were blended in such a ratio of black : blue : violet is 1:3:1 (by weight ratio). In

order to provide photosensitivity, 10% by weight (based on HEMA) of p-diazodiphenylamine was added.

[0040]

The above-mentioned photosensitive resist was coated on a non-alkaline glass substrate by a spin coater. Herein, a coating thickness was 0.8 μm , and a maximal transparency in visible light (700 nm) was 4.0%. Further, there is no uneven coating distribution and a good coating can be formed. The obtained coating was pre-baked at 50°C for 3 minutes, thereafter exposed by a high pressure mercury lamp through a fine test pattern by which resolution can be found at 300 mJ/cm^2 (for 1 minute). After exposure, development was carried out by means of a 1% aqueous malic acid solution.

[0041]

The formed pattern obtained by development at fine 10 μm lines was good without flowing out. Then, the above-mentioned black pixels were dyed under the following conditions.

dyestuff PC-Black 205D (made by Nippon Kayaku Co. Ltd.) 1.0% aqueous solution

pH 4.0

solution temperature 60°C

dipping 10 minutes

Maximal transparency of the coating after dyeing was 0.5% at 700 nm.

[0042]

(Comparative Example 2)

Black matrix having the same light shielding property as that of black matrix prepared in Example 2 was prepared without dyeing. That is, a coating thickness (1.5 μm) of the black photosensitive resinous composition similar to Example 2 was formed such that a maximal transparency in 700 nm was 0.5%, which was pre-baked and exposed (300 mJ/cm^2) and thereafter developed.

[0043]

The obtained pattern was flown out due to insufficient exposure, from which insufficient crosslinking is recognized. Then, by increasing the exposing amount to the point at which a 10 μm line of a test pattern was formed without flowing out, and the exposing amount was determined as 1500 mJ/cm^2 . As clear from the above-mentioned results, the black matrix prepared by using dyestuff and pigment can be prepared well at a low amount of irradiated ultra-violet.

[0044]

[Effect of the Invention]

According to the present invention, the following effects can be obtained.

- (1) Since a black dyestuff is used in together as a light shielding agent, a coating property on a substrate is improved compared with the case of using only a pigment and thus a coating without any uneven coating distribution can be obtained.

- (2) Since the black dyestuff is used, a coating having a low coating pressure can be obtained at a same light shielding property compared with the case of using only a pigment, which is advantageous when introduced into a liquid crystalline module.
- (3) Since an amount of ultraviolet ray irradiated is decreased, an irradiation time and an electric amount consumed are saved.